CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK, NEW YORK 10027

Transition Metal Borohydride Complexes. III.[1] The Structure of Octahydrotriboratobis(triphenylphosphine)copper(I)

BY STEPHEN J. LIPPARD[2] AND KENNETH M. MELMED[3]

Received June 2, 1969

The crystal and molecular structure of octahydrotriboratobis(triphenylphosphine)copper(I) has been determined by a three-dimensional X-ray crystallographic analysis. The colorless compound crystallizes in the monoclinic system, space group $P2_1/c$, with unit cell dimensions $a = 11.378$ (5) Å, $b = 20.66$ (1) Å, $c = 18.13$ (1) Å, $\beta = 127.05$ (5)°, and $Z = 4$. From ~2800 independent observable reflections collected by diffractometer, the structure was solved and has been refined by least-squares techniques to a final value for the discrepancy index, R, of 0.078. The crystal is composed of monomers in which the copper atom is coordinated to two triphenylphosphine ligands (Cu–P = 2.281 ± 0.007 Å, P–Cu–P = 120.0 ± 0.1°) and to two hydrogen atoms on different boron atoms of the $B_3H_8^-$ group (Cu–H = 1.84 ± 0.05 Å; H–Cu–H = 103 ± 2°). These structural features correlate well with results found for other bis(triphenylphosphine)copper(I) complexes and for the octahydrotriborate group in the $(OC)_4Cr(B_3H_8)^-$ anion. The geometries of the free and coordinated $B_3H_8^-$ ion are shown to be comparable. The infrared spectra of $L_2Cu(B_3H_8)$ complexes, where L is triphenylphosphine, triphenylarsine, or diphenylmethylphosphine, are discussed with reference to the known Cu–B_3H_8 attachment.

Introduction

The structural and chemical properties of transition metal borohydride complexes have been the subject of recent studies.[1,4] Because of their ready accessibility,[1,5,6] copper(I) complexes of general formula $L_2Cu(BH_4)$ have been the most thoroughly investigated. As described previously,[1] copper(I) complexes of the octahydrotriborate ion,[7,8] $B_3H_8^-$, were prepared in order to provide further information about the factors responsible for the stabilizing effect of certain ligands, notably triarylphosphines, on the copper–borohydride attachment. The structure of one such complex, $[(C_6H_5)_3P]_2Cu(B_3H_8)$, was of particular interest since the structure of the related borohydride complex is known.[4] In addition, since the $B_3H_8^-$ ion may be undergoing rapid intramolecular rearrangements in solution,[9] it seemed worthwhile to investigate whether its solid-state structure in the complex resembled that of the free octahydrotriborate ion.[10] The present paper provides definitive information on these points through a single-crystal X-ray diffraction study of $[(C_6H_5)_3P]_2Cu(B_3H_8)$. The mode of attachment of the octahydrotriborate ion to the copper atom conforms to the structural prototype previously found[8] for $(OC)_4Cr(B_3H_8)^-$.

Unit Cell and Space Group Determination

The compound $[(C_6H_5)_3P]_2Cu(B_3H_8)$ was prepared as reported previously[1] and recrystallized slowly from chloroform–ethanol. Optical examination showed the colorless crystals to have 2/m symmetry. Several crystals were mounted on the ends of glass fibers with hard shellac along the unique axis. After an approximate alignment on the optical goniometer, the crystals were tranferred to the Weissenberg and precession cameras for unit cell and space group determinations using Ni-filtered Cu K$\bar{\alpha}$ radiation (λ 1.5418 Å). The Laue symmetry 2/m and observed extinctions $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, uniquely suggested the space group to be $P2_1/c$ (no. 14),[11] a choice later proved correct by the successful refinement of the structure. The unit cell parameters were accurately determined by a least-squares technique in which the cell constants were refined to give the best fit between calculated and observed settings χ, ϕ, and 2θ for 21 independent reflections, carefully centered in the counter window of a Picker four-circle automated X-ray diffractometer.[12] The results are $a = 11.378 \pm 0.005$ Å, $b = 20.66 \pm 0.01$ Å, $c = 18.13 \pm 0.01$ Å, and $\beta = 127.05 \pm 0.05°$ at room temperature (*ca.* 23°). The computed cell volume ($V = 3400$ Å^3) and experimental density ($\rho = 1.19 \pm 0.02$ g/cm^3, measured by flotation in aqueous KI solutions) require four molecules per unit cell. The calculated density of 1.22 g/cm^3 is in reasonable agreement with that observed.

Collection and Reduction of Intensity Data

Intensity data were collected on the Picker diffractometer using a crystal which resembled an obliquely cut elliptical cylinder of approximate dimensions 0.20 × 0.15 × 0.23 mm, with an oblique angle of *ca.* 144°.

---

(1) Part II: S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, **7**, 1051 (1968).

(2) Alfred P. Sloan Foundation fellow.

(3) National Institutes of Health predoctoral trainee.

(4) S. J. Lippard and K. M. Melmed, *J. Am. Chem. Soc.*, **89**, 3929 (1967); *Inorg. Chem.*, **6**, 2223 (1967).

(5) J. M. Davidson, *Chem. Ind.* (London), 2021, (1964).

(6) F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965).

(7) The potential utility of this ion as a ligand for transition metal complexes was first drawn to our attention by a formal proposal of Mr. Peter Stokely (MIT, 1966) and has recently been demonstrated by other workers.[8]

(8) F. Klanberg and L. J. Guggenberger, *Chem. Commun.*, 1293 (1967); F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2272 (1968).

(9) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 132 (1959).

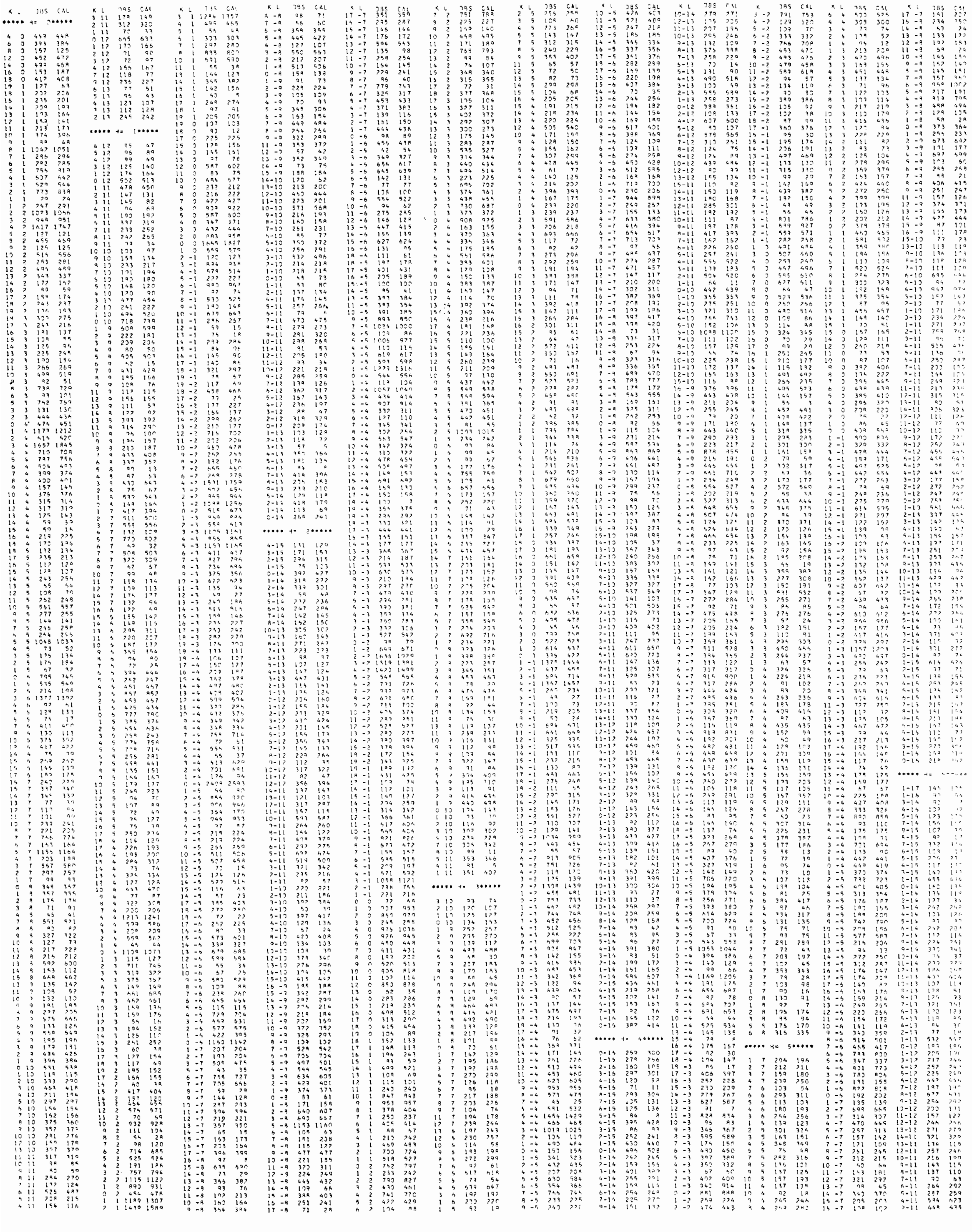
(10) C. R. Peters and C. E. Nordman, *J. Am. Chem. Soc.*, **82**, 5758 (1960).

(11) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1962, p 99.

(12) Programs for the IBM 7094 and 360-75 computers used in this work include local versions of: MODE-1, the Brookhaven diffractometer setting program and cell constant and orientation refinement program; GSET, the Prewitt diffractometer setting program: ACAC-3, a revised version of the Prewitt absorption correction and data reduction program; XDATA, the Brookhaven Wilson plot program; the Zalkin Fourier program, FORDAP; the Busing–Martin–Levy structure factor calculation and least-squares refinement program, OR-FLS; and the Busing–Martin–Levy error function program, OR-FFE.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (IN ELECTRONS × 10) FOR $[(C_6H_5)_3P]_2Cu(B_3H_8)$[a]



The crystal was mounted along the *b* axis. The mosaicity of the crystal was checked by ω scans for several high-angle reflections and found to be acceptable. Data were obtained with Ni-filtered Cu K$\bar{\alpha}$ radiation at 23 ± 2°. Experimental details are as reported previously[4] with the following changes: the scan range was 1.25° in 2θ plus the $K\alpha_1 - K\alpha_2$ difference, the takeoff angle was 2.4°, and the symmetrically varying re-

TABLE I (*Continued*)

K L	OBS	CAL
1-11	444	685
0-10	182	179
1-10	53	30
2-10	134	86
3-10	151	136
4-10	245	243
6-10	419	437
7-10	165	181
8-10	509	501
9-10	127	94
10-10	158	158
11-10	246	246
12-10	335	308
13-10	166	125
15-10	95	6
14 -9	341	359
13 -9	137	137
12 -9	191	165
11 -9	252	187
9 -9	95	9
8 -9	449	449
7 -9	145	147
5 -9	675	705
4 -9	492	483
3 -9	499	494
2 -9	488	499
1 -9	150	156
0 -8	555	548
1 -8	182	176
2 -8	114	47
3 -8	155	149
4 -8	151	179
5 -8	203	200
6 -8	562	596
8 -8	322	328
9 -8	233	254
10 -8	278	297
11 -8	394	386
12 -8	373	332
13 -8	195	200
14 -8	104	29
15 -8	147	96
16 -7	305	298
15 -7	153	128
14 -7	374	392
13 -7	172	155
12 -7	297	299
11 -7	243	244
10 -7	90	27
9 -7	120	97
8 -7	662	652
7 -7	252	256
6 -7	423	395
4 -7	178	148
3 -7	718	728
2 -7	751	797
1 -7	103	81
0 -6	558	550
1 -6	41	71
2 -6	150	118
3 -6	180	165
4 -6	498	492
5 -6	430	374
6 -6	428	437
7 -6	93	63
8 -6	191	167
9 -6	294	269
10 -6	168	111
11 -6	334	311
12 -6	114	39
13 -6	235	216
14 -6	142	83
15 -6	117	69
16 -6	154	158
16 -5	151	95
15 -5	135	48
14 -5	91	6
13 -5	218	247
12 -5	389	375
11 -5	527	515
10 -5	85	44
9 -5	320	294
8 -5	539	509
7 -5	150	146
6 -5	286	314
5 -5	314	290
4 -5	763	774
3 -5	293	304
2 -5	808	797
1 -5	340	332
0 -4	407	399
2 -4	111	97
3 -4	181	190
4 -4	720	708
5 -4	291	293
6 -4	260	255
7 -4	450	508
8 -4	107	109
9 -4	455	444
10 -4	273	275
11 -4	111	90
13 -4	237	248
14 -4	142	127
15 -4	91	5
16 -4	123	30
15 -3	164	113
14 -3	83	15
13 -3	404	395
12 -3	379	389
11 -3	513	523
10 -3	85	27
9 -3	577	577
8 -3	474	482
7 -3	218	221
6 -3	377	391
5 -3	283	240
4 -3	83	152
3 -3	55	57
1 -3	969	880
0 -2	742	709
1 -2	448	468
2 -2	227	221
3 -2	515	547
4 -2	176	149
5 -2	95	56
6 -2	132	96
7 -2	308	337
8 -2	150	139
9 -2	308	330
10 -2	288	286
11 -2	183	193
12 -2	171	169
13 -2	96	56
14 -2	115	72
15 -2	70	36
14 -1	204	222
13 -1	207	203
12 -1	235	210
11 -1	278	291
10 -1	67	58
9 -1	288	271
8 -1	208	193
7 -1	108	59
6 -1	201	177
5 -1	655	698
4 -1	304	317
3 -1	74	56
2 -1	125	120
1 -1	920	909
0 0	216	185
1 0	287	284
2 0	143	133
3 0	294	292
4 0	333	318
5 0	233	263
6 0	209	157
7 0	557	558
9 0	279	232
10 0	70	53
11 0	91	59
12 0	71	30
13 0	271	288
14 0	140	136
12 1	122	99
11 1	155	110
10 1	140	98
9 1	155	153
8 1	85	100
7 1	289	344
6 1	87	84
5 1	522	510
4 1	185	189
3 1	87	93
2 1	74	19
1 1	460	480
0 2	92	122
1 2	240	260
3 2	495	490
4 2	245	244
6 2	423	434
7 2	193	202
9 2	197	208
10 2	179	185
11 2	122	100
10 3	157	123
8 3	143	163
6 3	69	27
5 3	331	338
4 3	315	352
2 3	360	375
1 3	399	405
1 4	130	120
2 4	244	270
3 4	193	221
4 4	462	495
5 4	95	58
6 4	391	371
7 4	86	87
8 4	88	87
5 5	235	229
4 5	292	316
3 5	75	67
2 5	419	428
1 5	285	309
***** H= 7 *****		
1 3	294	317
2 3	111	30
3 3	353	367
4 3	147	143
5 3	479	477
7 2	337	340
6 2	100	18
4 2	111	58
3 2	188	183
2 2	100	110
1 2	182	172
0 2	175	149
1 1	407	403
2 1	62	10
3 1	170	177
4 1	213	240
5 1	396	390
6 1	333	324
7 1	247	245
8 1	156	131
9 1	328	316
10 1	133	78
11 0	79	46
10 0	73	83
9 0	289	296
8 0	155	146
7 0	349	377
6 0	85	5
5 0	94	97
4 0	52	11
3 0	193	205
2 0	353	357
1 0	224	210
0 0	393	408
1 -1	521	577
2 -1	383	359
3 -1	82	9
4 -1	94	92
5 -1	223	207
6 -1	519	538
7 -1	112	141
8 -1	238	218
9 -1	181	135
10 -1	97	81
11 -1	418	452
12 -1	119	105
13 -2	148	112
12 -2	297	296
11 -2	199	208
10 -2	304	312
9 -2	379	392
8 -2	211	365
7 -2	94	53
6 -2	159	171
5 -2	52	6
3 -2	340	310
2 -2	250	217
1 -2	182	197
0 -2	460	471
1 -3	660	681
2 -3	642	653
3 -3	271	259
4 -3	175	132
5 -3	137	139
6 -3	395	378
7 -3	105	71
8 -3	288	293
9 -3	116	99
10 -3	155	157
11 -3	282	301
13 -3	180	186
14 -4	125	88
13 -4	109	80
12 -4	414	404
11 -4	338	338
10 -4	312	342
9 -4	392	325
8 -4	130	145
7 -4	127	148
6 -4	220	235
5 -4	112	101
4 -4	324	310
3 -4	95	42
2 -4	189	183
1 -4	79	54
0 -4	472	438
1 -5	526	531
2 -5	579	587
3 -5	259	223
4 -5	320	332
5 -5	77	123
6 -5	139	137
7 -5	159	210
8 -5	277	276
9 -5	217	203
10 -5	182	188
11 -5	113	125
12 -5	124	127
13 -5	353	383
14 -5	181	190
14 -5	126	74
13 -6	90	21
12 -6	204	156
11 -6	354	296
10 -6	107	72
9 -6	247	267
8 -6	278	309
7 -6	120	65
6 -6	459	473
5 -6	252	232
4 -6	330	308
3 -6	215	195
2 -6	310	286
1 -6	95	104
0 -6	764	718
1 -7	95	64
2 -7	279	296
3 -7	339	356
4 -7	440	432
5 -7	277	279
6 -7	96	94
8 -7	427	422
9 -7	112	59
10 -7	244	213
11 -7	150	172
12 -7	211	214
13 -7	309	282
14 -7	342	409
16 -8	188	191
13 -8	98	48
12 -8	239	255
11 -8	275	286
10 -8	143	183
9 -8	142	99
8 -8	351	342
7 -8	335	300
6 -8	553	558
5 -8	172	143
4 -8	194	168
3 -8	156	161
2 -8	279	277
1 -8	279	300
0 -8	347	337
1 -9	175	160
2 -9	226	238
3 -9	258	281
4 -9	497	478
5 -9	353	377
6 -9	229	230
7 -9	252	241
8 -9	244	278
9 -9	178	171
10 -9	315	315
11 -9	205	213
13 -9	168	195
14 -9	385	388
14-10	95	10
13-10	73	88
12-10	391	373
11-10	194	163
9-10	78	37
8-10	527	565
7-10	67	44
6-10	313	281
5-10	177	191
4-10	189	217
3-10	321	321
2-10	101	5
1-10	103	115
0-10	99	89
1-11	264	260
2-11	279	275
3-11	118	111
4-11	348	367
5-11	241	269
6-11	179	151
7-11	408	411
10-11	407	467
11-11	199	198
12-11	148	163
13-11	111	119
12-12	191	211
11-12	94	111
9-12	206	187
8-12	451	463
7-12	81	81
6-12	336	351
5-12	256	263
3-12	173	144
2-12	98	126
1-12	125	133
0-12	372	350
1-13	245	283
2-13	70	14
3-13	70	23
4-13	198	207
5-13	124	97
6-13	111	105
7-13	321	381
8-13	213	250
9-13	184	135
10-13	105	120
11-13	404	425
10-14	83	24
9-14	386	398
8-14	175	166
7-14	170	37
6-14	362	374
5-14	157	136
4-14	114	36
3-14	99	62
2-14	155	147
0-14	229	230
1-15	348	387
3-15	105	101
6-15	85	16
7-15	244	256
9-15	124	101
6-16	120	69
5-16	100	66
4-16	135	122
2-15	106	64
0-16	123	107
1-17	405	433
2-17	75	42
***** H= 8 *****		
0-16	73	22
1-16	210	267
2-15	139	42
3-16	333	324
4-16	179	185
5-15	144	196
7-15	198	198
6-15	132	202
5-15	156	189
3-15	151	140
2-15	210	196
1-15	149	106
0-14	73	68
1-14	103	81
2-14	207	186
3-14	162	180
4-14	401	414
6-14	230	202
7-14	274	285
8-14	97	92
9-14	264	253
10-13	137	126
9-13	165	158
7-13	330	327
6-13	93	119
5-13	333	353
4-13	167	142
3-13	79	44
2-13	331	370
1-13	117	113
0-12	151	193
2-12	175	178
3-12	203	196
4-12	382	374
5-12	120	65
6-12	347	382
7-12	92	39
8-12	154	99
9-12	254	255
10-12	93	51
11-12	222	189
12-11	227	228
11-11	192	176
10-11	167	177
9-11	273	224
7-11	268	296
6-11	154	171
5-11	162	150
4-11	121	70
3-11	144	153
2-11	98	57
1-11	88	45
0-10	327	307
1-10	97	81
2-10	118	116
3-10	236	221
4-10	259	255
5-10	192	186
6-10	154	140
7-10	62	54
8-10	176	183
9-10	112	87
10-10	112	102
11-10	161	179
12-10	308	331
13 -9	174	155
12 -9	170	152
11 -9	135	122
10 -9	252	285
9 -9	70	51
8 -9	236	240
7 -9	259	272
6 -9	85	31
5 -9	212	248
4 -9	51	13
3 -9	65	127
2 -9	287	284
1 -9	89	114
0 -8	188	184
1 -8	95	51
2 -8	102	61
3 -8	110	107
4 -8	59	35
5 -8	277	269
6 -8	235	242
7 -8	125	132
8 -8	211	183
9 -8	155	87
10 -8	196	224
11 -8	121	108
12 -8	441	395
13 -8	83	19
13 -7	127	114
12 -7	127	123
11 -7	72	58
10 -7	298	326
9 -7	184	140
8 -7	98	115
7 -7	445	455
6 -7	170	200
5 -7	273	241
4 -7	244	241
3 -7	230	239
2 -7	454	446
1 -7	304	280
0 -6	322	347
1 -6	183	179
2 -6	285	256
3 -6	293	289
4 -6	90	64
5 -6	225	272
6 -6	338	348
7 -6	315	313
8 -6	418	404
9 -6	157	131
11 -6	84	25
12 -6	349	332
11 -5	250	238
10 -5	428	433
9 -5	190	210
8 -5	207	217
7 -5	109	66
6 -5	115	121
5 -5	210	262
4 -5	93	33
3 -5	291	224
2 -5	217	207
1 -5	335	327
0 -4	361	371
1 -4	110	92
2 -4	414	424
3 -4	159	139
4 -4	153	111
5 -4	187	177
6 -4	118	93
7 -4	124	78
8 -4	310	324
9 -4	229	241
10 -4	177	142
11 -4	150	156
12 -4	307	342
10 -3	414	389
9 -3	235	251
8 -3	285	295
7 -3	394	387
6 -3	77	98
5 -3	79	77
4 -3	159	150
3 -3	177	198
2 -3	299	314
1 -3	186	168
0 -2	696	685
1 -2	143	114
2 -2	312	253
4 -2	141	144
5 -2	266	258
6 -2	157	157
8 -2	96	86
9 -2	282	283
10 -2	155	164
9 -1	210	222
8 -1	297	301
7 -1	166	164
6 -1	90	87
5 -1	147	143
4 -1	95	48
3 -1	79	80
2 -1	117	103
1 -1	93	33
0 0	358	335
2 0	222	222
3 0	323	316
4 0	75	12
5 0	305	283
6 0	113	87
7 0	101	93
4 1	75	10
3 1	105	50
2 1	127	97
1 1	217	241
***** H= 9 *****		
5 -2	118	101
6 -2	75	26
2 -2	278	277
1 -2	109	86
0 -2	278	339
1 -3	97	52
2 -3	109	80
3 -3	95	38
4 -3	253	261
6 -3	76	21
5 -4	91	80
4 -4	172	141
3 -4	295	263
2 -4	339	336
1 -4	108	102
0 -4	230	172
1 -5	77	11
2 -5	206	153
3 -5	91	44
4 -5	80	105
5 -5	175	175
7 -5	314	286
8 -5	462	502
9 -5	278	309
10 -5	254	270
9 -6	109	63
7 -6	235	219
6 -6	255	218
5 -6	253	237
4 -6	119	108
3 -6	81	93
2 -6	275	226
1 -6	102	52
0 -6	447	403
1 -7	372	371
2 -7	92	31
3 -7	83	88
4 -7	178	232
5 -7	120	39
7 -7	138	89
8 -7	250	259
9 -7	82	45
10 -7	254	238
10 -8	230	180
9 -8	158	174
8 -8	95	53
5 -8	314	315
4 -8	170	156
3 -8	81	64
2 -8	230	205
0 -8	414	398
1 -9	201	206
2 -9	272	234
3 -9	80	71
5 -9	113	80
6 -9	253	241
7 -9	249	248
8 -9	176	199
9 -9	115	105
10 -9	122	65
9-10	230	245
8-10	151	157
7-10	123	134
6-10	243	216
5-10	170	99
4-10	300	296
3-10	193	185
2-10	175	183
1-10	179	170
0-10	471	425
1-11	128	89
2-11	318	304
3-11	215	229
4-11	197	177
5-11	391	393
6-11	156	163
7-11	460	453
8-11	95	62
9-11	197	206
10-11	108	28
9-12	149	137
7-12	92	73
6-12	314	341
5-12	139	154
4-12	308	302
3-12	397	425
1-12	275	270
0-12	147	127
1-13	135	147
2-13	260	225
3-13	176	198
4-13	245	251
5-13	440	452
6-13	134	180
7-13	338	363
8-13	130	87
7-14	178	178
6-14	138	115
5-14	121	66
4-14	237	255
3-14	342	327
2-14	91	112
1-14	294	328
0-14	105	106
1-15	381	432
3-15	135	139
4-15	249	292
5-15	219	219
2-16	202	211
1-16	327	358
0-16	94	72
***** H= 10 *****		
0-14	183	190
1-14	189	154
2-14	174	180
3-14	395	452
5-13	389	415
4-13	170	206
3-13	77	108
2-13	149	116
1-13	99	50
0-12	175	171
1-12	214	239
3-12	537	536
5-12	328	364
6-12	91	78
7-11	217	245
6-11	153	161
5-11	500	522
4-11	65	51
3-11	274	263
1-11	128	126
0-10	434	383
1-10	114	88
2-10	197	224
3-10	364	404
4-10	225	276
5-10	253	238
6-10	100	100
7-10	74	94
7 -9	225	232
5 -9	388	378
4 -9	105	50
3 -9	197	165
2 -9	137	145
1 -9	159	158
0 -8	584	621
2 -8	212	184
3 -8	91	107
4 -8	188	138
5 -8	241	235
6 -8	133	105
7 -8	191	184
6 -7	73	32
5 -7	226	204
4 -7	259	251
2 -7	237	226
1 -7	122	55
0 -6	426	423
1 -6	193	153
2 -6	226	240
3 -6	150	165
3 -5	97	56
2 -5	293	281
1 -5	84	74

[a] The calculated value of $F(000)$ is 13,050.

ceiving aperture was set to a 3.0 × 3.0 mm opening. Efficient data collection was achieved by programming the diffractometer to scan the shortest reciprocal lattice directions first, resulting in an over-all efficiency (including the standard reflections) of 70%. All of the independent reflections within the sphere $\theta \leq 48°$ were collected in a period of 6 days.

The raw data were corrected for background, use of attenuators, absorption, and Lorentz–polarization effects as indicated previously.[4] Absorption corrections ($\mu = 19.4$ cm^{-1}) calculated by the program ACAC were checked against an experimental measure of the change in peak intensity with ϕ for several reflections at $\chi = 90°$; excellent agreement was obtained. The transmission factors ranged from 0.50 to 0.75. The data were then placed on an approximately absolute scale through a modification of Wilson's method.[12] From the resultant values for $|F_o|$ and $|F_o|^2$, the structure was solved by the usual Patterson, Fourier, and least-squares refinement processes (see below). Scattering factor tables, appropriately corrected in the cases of copper and phosphorus for anomalous dispersion,[13] were obtained from the "International Tables for X-ray Crystallography."[14] Form factors used were for the neutral atoms. Weights, $w = \sigma(F)^{-2}$, were assigned to each reflection according to[15]

$$\sigma(F) = (LpT)^{-1/2}[(I + \sigma(I))^{1/2} - I^{1/2}]$$

where L, p, and T are the Lorentz, polarization, and transmission factors, respectively, I is the integrated intensity corrected for background and attenuators, and $\sigma(I)$ is the standard deviation of I, estimated[16] to be

$$\sigma(I) = [E + (T_E/2T_B)^2(B_1 + B_2) + (\epsilon I)^2]^{1/2}$$

In the above expression, E is the total counts in the peak plus background observed for a scan time T_E, B_1 and B_2 are the background counts observed for time T_B at each extreme of the scan, and ϵ is the "ignorance factor,"[16c] set equal to 0.03, to prevent excessively high weight being given to the strong reflections. Of the 3000 reflections, those for which $I \leq 2\sigma(I)$ were excluded from the refinement (~200 reflections). All subsequent calculations were performed on the remaining 2805 reflections.

Determination and Refinement of the Structure

Using the corrected data, an origin-removed, sharpened Patterson map was computed and solved for the positions of the copper and two phosphorus atoms, all in general positions (x, y, z) of the space group $P2_1/c$. A cycle of least-squares refinement of the over-all scale factor and positional parameters was then carried out and the results were used to determine the signs of the structure factors for a difference Fourier synthesis. From the Fourier map several light atoms were located and then used together with copper and phosphorus atoms to phase a second Fourier synthesis. A third iteration of this procedure yielded all 39 carbon and boron atoms in the asymmetric unit. Three cycles of least-squares refinement of the scale factor, atomic positional parameters, and isotropic thermal parameters resulted in convergence at values of 0.109 and

---

(13) See ref 11, Vol. III, p 213 ff.

(14) See ref 11, Vol. III, pp 202, 210.

(15) D. E. Williams and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 1660 (1964).

(16) (a) G. M. Brown and H. A. Levy, *J. Phys.* (Paris), **25**, 497 (1964); (b) R. D. Ellison and H. A. Levy, *Acta Cryst.*, **19**, 260 (1965); (c) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

TABLE II

FINAL PARAMETERS FOR $[(C_6H_5)_3P]_2Cu(B_3H_8)$[a,b]

Atomic Positional and Isotropic Thermal Parameters

Atom	x	y	z	B, Å^2
Cu	0.03954 (11)	0.08629 (5)	0.21997 (6)	. . .
P_1	0.20160 (20)	0.11736 (9)	0.19275 (12)	. . .
P_2	0.06844 (20)	−0.01109 (9)	0.28886 (12)	. . .
B_1	−0.2556 (14)	0.1283 (7)	0.1925 (9)	. . .
B_2	−0.0895 (11)	0.1692 (5)	0.2266 (7)	. . .
B_3	−0.1958 (11)	0.1271 (5)	0.1213 (7)	. . .
CA1	0.1306 (7)	0.1752 (3)	0.0988 (4)	3.7 (2)
CA2	0.0539 (11)	0.2266 (5)	0.0965 (6)	4.4 (2)
CA3	−0.0032 (12)	0.2742 (5)	0.0244 (8)	6.8 (3)
CA4	0.0245 (12)	0.2690 (6)	−0.0368 (8)	7.3 (3)
CA5	0.1003 (11)	0.2179 (5)	−0.0373 (7)	7.9 (3)
CA6	0.1528 (11)	0.1698 (5)	0.0334 (7)	6.4 (2)
CB1	0.3631 (7)	0.1590 (3)	0.2895 (4)	3.3 (1)
CB2	0.3979 (9)	0.1516 (4)	0.3771 (5)	4.3 (2)
CB3	0.5221 (9)	0.1834 (4)	0.4539 (6)	5.3 (2)
CB4	0.6068 (10)	0.2205 (5)	0.4402 (7)	6.1 (2)
CB5	0.5761 (10)	0.2294 (5)	0.3573 (7)	6.1 (2)
CB6	0.4503 (9)	0.1986 (4)	0.2797 (6)	5.0 (2)
CC1	0.2701 (7)	0.0517 (3)	0.1615 (4)	3.0 (1)
CC2	0.4084 (9)	0.0500 (4)	0.1826 (5)	4.3 (2)
CC3	0.4509 (10)	−0.0015 (4)	0.1539 (6)	5.1 (2)
CC4	0.3551 (10)	−0.0527 (5)	0.1059 (6)	5.4 (2)
CC5	0.2175 (10)	−0.0523 (4)	0.0856 (6)	5.0 (2)
CC6	0.1748 (9)	−0.0003 (4)	0.1144 (5)	4.1 (2)
CD1	0.1273 (7)	−0.0077 (3)	0.4072 (4)	3.1 (1)
CD2	0.0998 (8)	0.0477 (4)	0.4381 (5)	3.9 (2)
CD3	0.1472 (8)	0.0521 (4)	0.5290 (5)	4.2 (2)
CD4	0.2150 (9)	−0.0004 (4)	0.5878 (6)	4.7 (2)
CD5	0.2453 (10)	−0.0539 (5)	0.5602 (6)	5.2 (2)
CD6	0.2015 (8)	−0.0593 (4)	0.4691 (5)	4.5 (2)
CE1	0.2068 (7)	−0.0644 (3)	0.3016 (5)	3.5 (2)
CE2	0.3480 (9)	−0.0415 (4)	0.3481 (5)	4.6 (2)
CE3	0.4572 (12)	−0.0810 (5)	0.3563 (7)	6.6 (2)
CE4	0.4242 (12)	−0.1428 (5)	0.3218 (7)	6.6 (2)
CE5	0.2868 (11)	−0.1657 (5)	0.2763 (6)	6.3 (2)
CE6	0.1754 (11)	−0.1275 (4)	0.2656 (6)	5.2 (2)
CF1	−0.0971 (7)	−0.0602 (3)	0.2265 (5)	3.3 (1)
CF2	−0.1916 (9)	−0.0578 (4)	0.1309 (5)	4.4 (2)
CF3	−0.3159 (9)	−0.0970 (4)	0.0788 (6)	5.1 (2)
CF4	−0.3474 (11)	−0.1391 (5)	0.1219 (7)	5.6 (2)
CF5	−0.2605 (11)	−0.1429 (5)	0.2157 (7)	6.3 (2)
CF6	−0.1334 (10)	−0.1032 (4)	0.2674 (7)	5.2 (2)
H1	−0.252 (11)	0.083 (5)	0.238 (7)	13.0 (3.0)
H2	−0.340 (11)	0.155 (5)	0.170 (7)	10.0 (3.0)
H3	−0.146 (9)	0.172 (4)	0.269 (6)	7.0 (3.0)
H4	−0.090 (6)	0.218 (3)	0.208 (4)	3.0 (1.0)
H5	0.023 (6)	0.148 (2)	0.285 (3)	2.0 (1.0)
H6	−0.144 (5)	0.084 (3)	0.109 (3)	3.0 (1.0)
H7	−0.252 (9)	0.159 (4)	0.061 (6)	10.0 (2.0)
H8	−0.312 (9)	0.104 (4)	0.099 (5)	8.0 (2.0)

Anisotropic Thermal Parameters ($\times 10^3$)[c]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	10.1 (2)	1.38 (3)	3.54 (6)	0.18 (6)	3.69 (8)	0.09 (3)
P1	11.0 (3)	1.55 (5)	4.05 (11)	0.01 (10)	3.99 (15)	0.23 (6)
P2	10.5 (3)	1.64 (6)	3.33 (10)	−0.10 (10)	3.46 (15)	0.16 (6)
B1	17.5 (2.1)	5.0 (5)	8.0 (8)	8.8 (8)	8.3 (1.2)	−0.3 (5)
B2	14.5 (1.7)	2.0 (3)	5.9 (6)	1.7 (6)	5.6 (9)	0.7 (3)
B3	11.7 (1.6)	2.6 (3)	4.5 (6)	0.6 (6)	2.3 (8)	−0.1 (3)

0.125 for the discrepancy factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, respectively.

Examination of a difference Fourier map at this point indicated several possible hydrogen atom peaks and some nonisotropic thermal motion for all atoms, but especially the copper and phosphorus atoms. Because of computer storage limitations, it was decided to continue refinement assigning anisotropic thermal parameters of the form

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$$

TABLE II (*Continued*)

Phenyl Ring Hydrogen Atom Positional Parameters[d]

Atom[e]	x	y	z	Atom[e]	x	y	z
A2	0.038 (7)	0.237 (3)	0.144 (5)	D2	0.048 (7)	0.082 (3)	0.396 (4)
A3	−0.036 (7)	0.294 (3)	0.042 (4)	D3	0.121 (8)	0.094 (4)	0.547 (5)
A4	−0.060 (14)	0.305 (6)	−0.085 (9)	D4	0.236 (8)	0.003 (4)	0.654 (6)
A5	0.117 (10)	0.215 (6)	−0.085 (9)	D5	0.294 (10)	−0.091 (4)	0.591 (6)
A6	0.220 (9)	0.143 (4)	0.038 (5)	D6	0.228 (7)	−0.094 (3)	0.442 (4)
B2	0.443 (6)	0.200 (3)	0.229 (4)	E2	0.369 (7)	0.004 (3)	0.385 (4)
B3	0.622 (11)	0.256 (5)	0.334 (7)	E3	0.516 (7)	−0.064 (3)	0.406 (5)
B4	0.661 (10)	0.239 (4)	0.502 (7)	E4	0.506 (14)	−0.172 (6)	0.332 (8)
B5	0.513 (8)	0.174 (3)	0.501 (5)	E5	0.246 (10)	−0.215 (5)	0.239 (6)
B6	0.336 (9)	0.118 (4)	0.382 (5)	E6	0.088 (11)	−0.132 (5)	0.213 (7)
C2	0.471 (8)	0.088 (4)	0.212 (5)	F2	−0.087 (6)	−0.104 (2)	0.324 (4)
C3	0.568 (9)	−0.004 (4)	0.170 (5)	F3	−0.270 (16)	−0.176 (8)	0.244 (10)
C4	0.383 (10)	−0.095 (5)	0.078 (6)	F4	−0.421 (12)	−0.165 (5)	0.080 (7)
C5	0.139 (9)	−0.085 (4)	0.063 (6)	F5	−0.391 (9)	−0.087 (4)	0.006 (6)
C6	0.077 (8)	0.000 (3)	0.101 (5)	F6	−0.168 (6)	−0.029 (3)	0.094 (4)

[a] See Figures 1 and 2 for the atom-labeling scheme. [b] Standard deviations, in parentheses beside each entry, occur in the last significant figure for each parameter as derived from the inverse matrix of the final least-squares refinement cycle. [c] The form of the anisotropic thermal ellipsoid is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [d] Thermal parameters for these atoms ranged from 3 to 20 ± 4 Å^2, with an average of 9 Å^2. [e] Atoms are labeled to correspond to their respective carbon atoms (Figure 1).

to the copper, phosphorus, and boron atoms, and isotropic temperature factors to all other atoms. The boron atoms were refined anisotropically in order to provide the best conditions for locating the hydrogen atoms of the $B_3H_8^-$ group. Difference Fourier maps calculated after this refinement again showed evidence for nonisotropic thermal motion of the carbon atoms but, in addition, revealed 32 peaks, with an average peak height of 0.65 e$^-$/Å^3, in the regions where the 38 missing H atoms were expected to occur. Hydrogen atoms of the $B_3H_8^-$ group were quite distinct ($\sim$0.7 e$^-$/Å^3) at this stage.

Subsequent structure factor calculations and least-squares refinements were carried out in which the Cu, P, and B positional and anisotropic thermal parameters and the C and octahydrotriborate hydrogen positional and isotropic thermal parameters were varied. Thermal parameters for the phenyl ring hydrogen atoms were initially assigned the same values as those of the carbon atoms to which they were attached and their atomic coordinates were changed by the amount of change in the positions of the corresponding carbon atoms. Since it was still not possible to find the six remaining phenyl hydrogen atoms, these were placed into the structure in accordance with the well-known stereochemistry of such groups, using a C–H distance of 1.0 Å. Refinement of Cu, P, and B anisotropically and the 74 other atoms isotropically, carried out in phases because of computer space limitations, led to final values of $R_1 = 0.078$ and $R_2 = 0.079$. R_1 including *all* 3000 reflections was 0.087. A final difference Fourier map showed a peak of 0.7 e$^-$/Å^3 at the Cu atom position and peaks of $\sim$0.5 e$^-$/Å^3 near the phenyl rings. In view of the large number (80) of independent atoms, however, anisotropic refinement of carbon atom parameters was not pursued. The estimate of the standard deviation of an observation of unit weight was 1.79. Table I contains the final list of calculated and observed structure factors. In Table II are summarized the final atomic positional and thermal parameters for all atoms, together with their standard deviations as estimated from the inverse matrix of the final least-squares refinement cycle. The refinement of the hydrogen atoms of the $B_3H_8^-$ group is judged to be more significant than that of the phenyl ring hydrogen atoms, since boron but not carbon atoms were refined anisotropically. Refined positional parameters for individual phenyl hydrogen atoms are included in Table II.

Description and Discussion of the Structure

Octahydrotriboratobis(triphenylphosphine)copper(I) crystallizes as monomeric units with the structure shown schematically in Figures 1 and 2. Of primary interest is the mode of coordination of the $B_3H_8^-$ group to the copper atom through terminal hydrogen atoms on two different boron atoms. As evident from Figure 2, this is achieved by canting the plane of the three boron atoms at an angle of 123° with respect to the plane defined by the H5–Cu–H6 bond angle. The five-membered chelate ring containing atoms Cu, H5, B2, B3, and H6 is not strictly planar, being folded slightly about the line joining H5 and H6. These two hydrogen atoms are situated 0.38 and 0.40 Å, respectively, above the plane defined by the copper and two boron atoms. The observed structural attachment appears to be the preferred one for $B_3H_8^-$ complexes; it has also been found to occur in the $(OC)_4Cr(B_3H_8)^-$ ion and is thought to exist in several related molecules.[8]

A summary of the geometric features of the copper coordination sphere is contained in Table III. For comparison purposes, selected results for the related borohydride,[4] nitrate,[17] and trifluoroacetylacetonate[18] complexes are included in the table. The average Cu–P distance and P–Cu–P angle in the $B_3H_8^-$ complex are comparable to similar values obtained for the BH_4^- compound. As before,[4] the angle has opened up considerably from an idealized tetrahedral value,

---

(17) G. G. Messmer and G. J. Palenik, *Can. J. Chem.*, **47**, 1440 (1969).
(18) M. Bartlett and G. J. Palenik, *Acta Cryst.*, **A25**, S173 (1969).

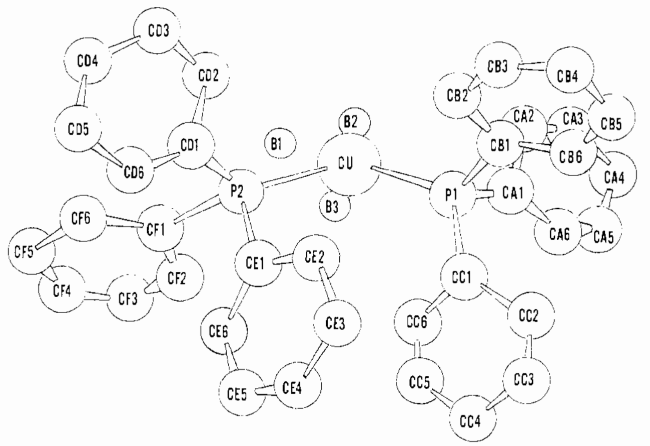


Figure 1.—Perspective drawing of the molecule indicating the atom-labeling scheme. Hydrogen atoms are not shown (see Figure 2).

and the effect is even greater in the nitrate and trifluoroacetylacetonate analogs. Previous considerations[4] have shown that steric interactions between the triphenylphosphine ligands are not likely to be the sole cause of the large observed P–Cu–P angle. For example, the increase of the P–Cu–P angle from an idealized value of 109.5° to observed values of >120° may be rationalized by considering repulsions between electron pairs bonded to the copper atom.[19-21] For the homologous series of compounds listed in Table III, the P–Cu–P angle is seen to increase with increasing electronegativity of the donor atoms of the group X. In terms of the electron-pair repulsion theory,[20] an increase in the electronegativity of a ligand will cause a decrease in the size of the bonding orbital(s) between that ligand and the central atom. In the present case, more space is made available for expansion of the P–Cu–P bond angle.[22] The results of crystal structure analyses of diphenylmethylphosphinecopper(I) complexes, currently in progress,[23] should provide further delineation of the stereochemical and electronic factors responsible for the P–Cu–P angles observed in $[(C_6H_5)_3P]_2CuX$ compounds.

Although the standard deviations in the individual values are large, it is of interest that the average Cu–H distance in $[(C_6H_5)_3P]_2Cu(B_3H_8)$ is approximately 3σ less than the corresponding distance in $[(C_6H_5)_3P]_2Cu(BH_4)$ (Table III). The Cu–H bonds in the $B_3H_8^-$ complex are part of a five-membered chelate ring (Figure 1) whereas in $[(C_6H_5)_3P]_2Cu(BH_4)$, the Cu–H bonds participate in a four-membered ring. In the borohydride compound, copper–hydrogen orbital overlap is

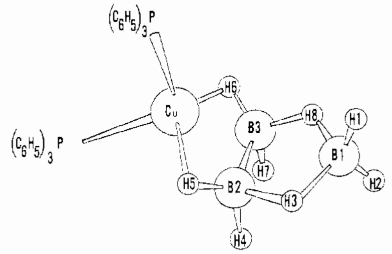


Figure 2.—Sketch of the structure showing the mode of attachment of the $B_3H_8^-$ ion to the copper atom and the hydrogen-atom-labeling scheme.

TABLE III

GEOMETRY OF THE COPPER COORDINATION SPHERE IN $[(C_6H_5)_3P]_2CuX$ COMPLEXES[a]

Distance	Value, Å	Angle	Value, deg
		X = B_3H_8[b]	
Cu–P1	2.274 (2)	P1–Cu–P2	119.97 (7)
Cu–P2	2.288 (2)	P1–Cu–H5	111 (2)
Cu–H5	1.84 (5)	P1–Cu–H6	108 (1)
Cu–H6	1.85 (5)	P2–Cu–H5	107 (2)
Cu–B2	2.30 (1)	P2–Cu–H6	106 (2)
Cu–B3	2.30 (1)	H5–Cu–H6	103 (2)
		Cu–H5–B2	100 (3)
		Cu–H6–B3	98 (3)
		X = BH_4[c]	
Cu–P	2.276 (1)	P–Cu–P′	123.26 (6)
Cu–H	2.02 (5)	H–Cu–H	69 (3)
Cu–B	2.18 (1)	P–Cu–H (av)	114
		X = $CF_3COCHCOCH_3$[d]	
Cu–P	2.25	P–Cu–P	127
		X = NO_3[e]	
Distances not given		P–Cu–P	131.1
		O–Cu–O	57.5

[a] Numbers given in parentheses refer to the standard deviation in the last significant figure listed. [b] See Figures 1 and 2 for atom-labeling scheme. [c] Reference 4. [d] Reference 18. [e] Reference 17.

reduced by the constraint of the small ring (H–Cu–H angle of 69°), and the Cu–H bond lengths are correspondingly greater. A similar effect has been previously noted[24] for an iron–sulfur complex containing both sized chelate rings and may be a general phenomenon. Although the possibility of direct Cu–B bonding exists for $[(C_6H_5)_3P]_2Cu(BH_4)$,[4] it can probably be ruled out for $[(C_6H_5)_3P]_2Cu(B_3H_8)$, in which the observed Cu–B distances are significantly larger (Table III).

Table IV summarizes the geometry of the octahydrotriborate ion in $[(C_6H_5)_3P]_2Cu(B_3H_8)$. As depicted in Figure 2, the bridging hydrogen atoms H3 and H8 are not strictly coplanar with the three boron atoms. The ring is slightly puckered with H3 +0.2 Å and H8 −0.8 Å out of the plane defined by the boron atoms. Within the limits of error, the average structural features are in excellent agreement with the results of two other X-ray diffraction studies of the $B_3H_8^-$ ion (Table V). As evident from Table V, the two bridging hydrogen atoms H_b are 0.3–0.4 Å closer to

---

(19) This argument was suggested to us by Professor R. J. Gillespie (private communication) for the case of $[(C_6H_5)_3P]_2Cu(BH_4)$. Explanations involving Cu–P dπ–dπ or pπ–dπ bonding[21] are also possible.

(20) R. J. Gillespie, *Angew. Chem. Intern. Ed. Engl.*, **6**, 819 (1967), and references contained therein.

(21) S. Ahrland and J. Chatt, *Chem. Ind.* (London), 96 (1955).

(22) The size of the chelate ring opposite the P–Cu–P bond angle may also be a factor in the case of two ligands X with donor atoms of comparable electronegativity. Thus, the four-membered ring in the borohydride complex allows the angle to expand more than does the five-membered chelate of the octahydrotriborate complex.

(23) S. J. Lippard, D. Stowens, and D. A. Ucko, to be submitted for publication.

(24) D. Coucouvanis and S. J. Lippard, *J. Am. Chem. Soc.*, **91**, 307 (1969).

TABLE IV

GEOMETRY OF THE OCTAHYDROTRIBORATE GROUP IN $[(C_6H_5)_3P]_2Cu(B_3H_8)$[a]

Interatomic Distances

Distance	Value, Å	Distance	Value, Å
B1–B2	1.83 (2)	B2–H3	1.16 (9)
B2–B3	1.76 (1)	B2–H4	1.12 (6)
B1–B3	1.81 (2)	B2–H5	1.18 (6)
B1–H1	1.3 (1)	B3–H6	1.24 (5)
B1–H2	1.0 (1)	B3–H7	1.08 (9)
B1–H3	1.51 (9)	B3–H8	1.15 (8)
B1–H8	1.53 (8)		

Interbond Angles

Angle	Value, deg	Angle	Value, deg
H1–B1–H2	110 (7)	H4–B2–B3	105 (3)
H1–B1–H3	100 (6)	H5–B2–B3	118 (3)
H1–B1–H8	108 (6)	B2–B3–H6	120 (2)
H3–B1–H8	144 (5)	B2–B3–H7	113 (4)
H2–B1–H8	94 (6)	B2–B3–H8	117 (4)
H2–B1–H3	96 (7)	H6–B3–H7	108 (5)
B1–H3–B2	81 (5)	H6–B3–H8	102 (4)
H3–B2–H4	103 (5)	H7–B3–H8	93 (5)
H3–B2–H5	99 (4)	B3–H8–B1	82 (5)
H3–B2–B3	115 (4)		
H4–B2–H5	117 (4)		

[a] See footnotes *a* and *b* of Table III.

TABLE V

SUMMARY OF SELECTED AVERAGE STRUCTURAL FEATURES OF THE $B_3H_8^-$ GROUP[a]

	Distance, Å		
Bond[b]	$[(C_6H_5)_3P]_2Cu(B_3H_8)$	$(OC)_4Cr(B_3H_8)^-$ [c]	$B_3H_8^-$ [d]
B_1–H_t	1.2 (1)	1.2 (1)	1.05–1.20
B_1–H_b	1.52 (9)	1.43 (7)	1.5
B_2–H_b	1.15 (9)	1.15 (7)	1.2
B_2–H_t	1.10 (8)	1.07 (7)	1.05–1.20
B_2–H_m	1.21 (6)	1.29 (6)	*e*
B_2–B_3	1.76 (1)	1.78 (1)	1.80
$B_1\cdots B_2$	1.82 (2)	1.82 (1)	1.77

	Angle, deg		
Angle[b]	$[(C_6H_5)_3P]_2Cu(B_3H_8)$	$(OC)_4Cr(B_3H_8)^-$ [c]	$B_3H_8^-$
H_b–B_1–H_b	144 (5)	134 (5)	*e*
B_1–H_b–B_2	82 (5)	89 (4)	*e*
H_b–B_2–B_3	116 (4)	112 (3)	*e*
H_m–B_2–B_3	119 (3)	112 (3)	*e*
H_b–B_2–H_t	101 (5)	110 (5)	*e*
H_t–B_2–H_m	112 (5)	115 (4)	*e*

[a] See footnotes *a* and *b* of Table III. [b] H_t = terminal hydrogen; H_b = hydrogen bridging two boron atoms; H_m = hydrogen bridging boron and metal atoms; B_1 = unique boron atom (B1 in Figure 2); B_2 = nonunique boron atom (B2, B3 in Figure 2). [c] Reference 8; L. J. Guggenberger, *Inorg. Chem.*, in press. [d] Reference 10. [e] Value not reported.

the two symmetry-equivalent boron atoms B2 and B3 than to the unique boron atom, B1. This suggests that more negative charge resides on boron atoms B2 and B3 than on B1, a result consistent with calculated charge distributions for the $B_3H_8^-$ ion[25] and with the use of hydrogen atoms on B2 and B3, rather than those on B1, for metal complex formation.

Dimensions for the triphenylphosphine ligands are summarized in Table VI. The mean P–C distance, 1.822 Å, C–C distance, 1.39 Å, Cu–P–C angle, 114.8°, and C–P–C angle, 103.8°, are consistent with the values commonly found for coordinated triphenylphosphine ligands.[4,26] Since the standard deviation of the mean for C–C bond distances is sometimes greater than the individual esd's derived from the least-squares refinement (Table VI), the latter are judged to be less meaningful. Each of the phenyl rings is planar within the limits of experimental error. The relative orientation of these rings is shown in Figure 1.

TABLE VI

DIMENSIONS OF THE TRIPHENYLPHOSPHINE GROUP[a,b]

Bond	Length, Å	Angle	Value, deg	Angle	Value, deg
P1–CA1	1.829 (8)	Cu–P1–CA1	115.3 (2)	CA1–P1–CB1	102.2 (3)
P1–CB1	1.820 (7)	Cu–P1–CB1	113.9 (2)	CA1–P1–CC1	103.3 (3)
P1–CC1	1.819 (7)	Cu–P1–CC1	114.5 (2)	CB1–P1–CC1	106.2 (3)
P2–CD1	1.825 (6)	Cu–P2–CD1	116.1 (2)	CD1–P2–CE1	101.5 (3)
P2–CE1	1.821 (7)	Cu–P2–CE1	115.4 (2)	CD1–P2–CF1	105.1 (3)
P2–CF1	1.817 (7)	Cu–P2–CF1	113.5 (2)	CE1–P2–CF1	103.6 (3)

C–C bond distances, Å				C–C–C bond angles, deg			
Min	Max	Mean	σ mean	Min	Max	Mean[c]	Ring
1.33 (1)	1.44 (1)	1.39	0.04	117 (1)	123 (1)	120	A
1.34 (1)	1.42 (1)	1.39	0.03	118 (1)	123 (1)	120	B
1.38 (1)	1.40 (1)	1.39	0.01	119 (1)	120 (1)	120	C
1.34 (1)	1.41 (1)	1.39	0.02	118 (1)	120 (1)	120	D
1.34 (1)	1.41 (1)	1.40	0.03	119 (1)	121 (1)	120	E
1.36 (1)	1.42 (1)	1.38	0.02	116 (1)	122 (1)	120	F

[a] See footnotes *a* and *b* of Table III. [b] C–H bond lengths range from 0.8 to 1.2 Å, with an average value of 1.0 ± 0.1 Å. [c] Since the rings are all planar within the limits of error, a mean value of 120° is required by geometry.

Table VII lists the root-mean-square amplitudes of vibration for the six atoms refined anisotropically. The magnitudes (0.17–0.34 Å) and distribution of these values among the atoms are reasonable, indicating that the thermal parameters have physical significance. For example, the thermal ellipsoid for the B1 atom is somewhat larger than the corresponding ellipsoids for atoms B2 and B3, as would be expected from the observed attachment of the $B_3H_8^-$ ion to the copper atom.

TABLE VII

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)[a]

Atom[b]	Min	Intermed	Max
Cu	0.172	0.191	0.207
P1	0.180	0.195	0.223
P2	0.178	0.209	0.210
B1	0.23	0.29	0.34
B2	0.18	0.25	0.27
B3	0.20	0.23	0.29

[a] Taken along the principal axes of the thermal ellipsoids. The orientations of these axes may be worked out from the data of Table II and the unit cell parameters. [b] See Figure 1 for the atom-labeling scheme.

Infrared Spectral Studies

The solid-state (Nujol mull) and chloroform solution infrared spectra of $[(C_6H_5)_3P]_2Cu(B_3H_8)$ in the B–H

---

(25) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, Table 3-16, p 110.

(26) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc., A*, 2970 (1968), and references cited therein.

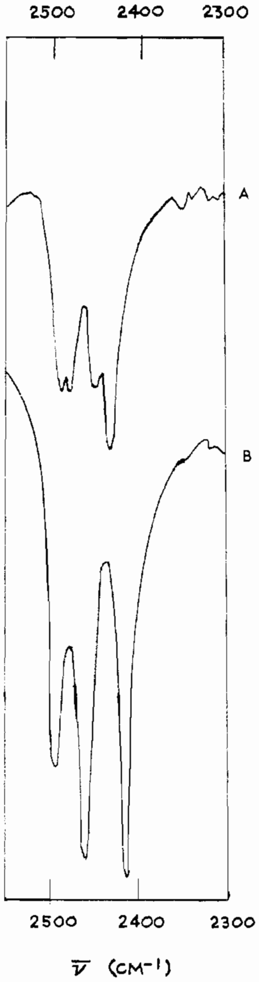


Figure 3.—Infrared spectra in the terminal B–H stretching frequency region of (A) $[(C_6H_5)_2CH_3P]_2Cu(B_3H_8)$ and (B) $[(C_6H_5)_3P]_2Cu(B_3H_8)$, both mulled in Nujol.

stretching frequency region have been reported previously.[1] The presence of three strong bands (Figure 3) in the mull spectrum between 2400 and 2500 cm^{-1}, where *terminal* B–H stretching vibrations are known to occur, was originally used to assign a structure to the complex in which the site symmetry of the Cu–B_3H_8 attachment was C_{2v}.[27] The correct structure (Figure 2) has approximate C_s site symmetry and requires four terminal B–H stretching modes. Two of these presumably have nearly identical energies, giving rise to the observed three bands. Recently the related complex $[(C_6H_5)_2CH_3P]_2Cu(B_3H_8)$ has been synthesized and its solid-state infrared spectrum was recorded.[23] As shown in Figure 3, four bands occur in the terminal B–H stretching frequency region, which is consistent with (but does not prove) a structure similar to that found for the triphenylphosphine complex. As with $[(C_6H_5)_3P]_2Cu(B_3H_8)$ and $[(C_6H_5)_3As]_2Cu(B_3H_8)$,[1] however, the infrared spectrum of $[(C_6H_5)_2CH_3P]_2Cu(B_3H_8)$ in chloroform solution shows only two broad, overlapping bands. One possible explanation for the difference between the solid-state and solution spectra is that a structural rearrangement has occurred. Attempts to investigate this possibility further by means of proton and ^{11}B nuclear magnetic resonance have thus far not been definitive. The proton nmr spectrum of $[(C_6H_5)_3P]_2Cu(B_3H_8)$ in chloroform at 32° shows a broad structureless line (width at half-height, 80 Hz) centered at τ 9.5 ppm which sharpens slightly at temperatures down to $-28°$. Below this temperature solubility becomes a problem. A study of the ^{11}B nmr spectrum under similar conditions showed only a broad peak without structure, a result also obtained by other investigators.[8]

Acknowledgments.—We thank the National Science Foundation for support of this research under Grants GP-6758 and GP-10737, Dr. D. F. Gaines for obtaining ^{11}B nmr spectra, Mr. D. A. Ucko for experimental assistance, and Dr. L. J. Guggenberger for communicating the results of his study prior to publication.

[27] S. J. Lippard and D. A. Ucko, *Chem. Commun.*, 983 (1967).