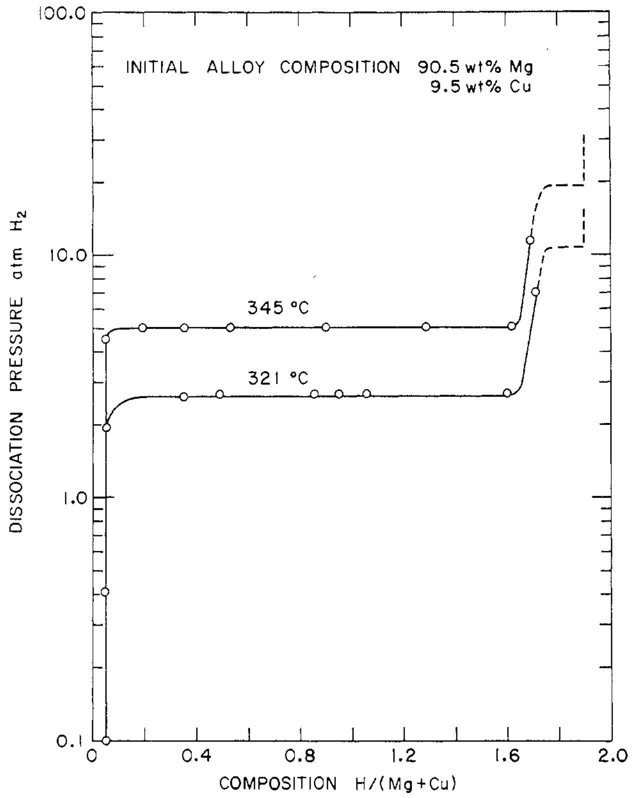


Figure 5.—Pressure–composition isotherm for the system 90.5 wt % Mg–9.5 wt % Cu–H_2.

In order to obtain a further check on the validity of eq 1 and 2, several alloys of various compositions were hydrided and dehydrided several times and then finally contacted with H_2 for several days. The H_2 pressure over the alloy was held 200 psi above the hydride dissociation pressure. These samples were analyzed for hydrogen content, and, as shown in Table I, the actual hydrogen contents are in good agreement with predicted values.

TABLE I

MAXIMUM HYDROGEN CONTENT OF Mg–Cu ALLOYS

Alloy composition,[a] wt %	Predicted value			Actual value		
	H/(Mg + Cu)	H/Mg	Wt % H	H/(Mg + Cu)	H/Mg	Wt % H
44.1 Mg 56.1 Cu	1.02	1.51	2.69	1.03	1.53	2.72
44.1 Mg 56.2 Cu	1.02	1.51	2.69	0.96	1.42	2.53
55.0 Mg 45.0 Cu	1.28	1.69	3.71	1.28	1.69	3.71
52.0 Mg 48.1 Cu	1.22	1.65	3.43	1.15	1.56	3.25
90.5 Mg 9.5 Cu	1.88	1.96	6.85	1.82	1.88	6.62

[a] By wet analysis.

Acknowledgment.—The authors wish to thank Dr. Warren E. Winsche for his interest and encouragement and Mr. Jonathan Hughes for his expert assistance in the laboratory.

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

Transition Metal Borohydride Complexes. I. The Solid-State Structure of Borohydridobis(triphenylphosphine)copper(I)

BY STEPHEN J. LIPPARD AND KENNETH M. MELMED

Received June 13, 1967

The crystal and molecular structure of borohydridobis(triphenylphosphine)copper(I) has been determined by a three-dimensional X-ray crystallographic analysis. The compound crystallizes as colorless needles in space group C2/c with unit cell dimensions a = 24.64, b = 9.058, c = 15.43 A, β = 116.2°, Z = 4. From 1750 independent observable reflections collected on a full-circle automated diffractometer, the structure was solved by use of conventional Patterson, Fourier, and least-squares refinement techniques. All atoms including hydrogen were located and refined to final values of the discrepancy indices of R_1 = 0.059 and R_2 = 0.044. The coordination geometry of the copper atom is quasi-tetrahedral, with two hydrogen atoms of the borohydride group bridging the copper and boron atoms. The resultant distances—Cu–P = 2.276 ± 0.001, Cu–B = 2.184 ± 0.009, Cu–H = 2.02 ± 0.05, $(B\text{–}H)_{av}$ = 1.31 ± 0.05 A—and angles—P–Cu–P′ = 123.26 ± 0.06, P–Cu–B = 118.4 ± 0.1°—suggest delocalized bonding between the copper atom and the borohydride group in which direct Cu–B overlap might be significant.

Introduction

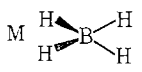
In 1949, Hoekstra and Katz prepared the first transition metal borohydride complexes by allowing metal (Ti, Hf, Th) halides to react with lithium borohydride or aluminum borohydride.[1] Since that time, a number of workers have succeeded in isolating compounds containing BH_4^- bonded to a transition metal.[2-13] Characteristically, these complexes are nondissociative in solution, decompose at various temperatures to form the free metal and numerous other products both in

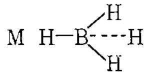
---

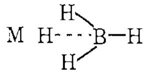
(1) H. R. Hoekstra and J. J. Katz, *J. Am. Chem. Soc.*, **71**, 2488 (1949).
(2) R. Nöth and R. Hartwimmer, *Chem. Ber.*, **93**, 2238 (1960).
(3) R. B. King, *Z. Naturforsch.*, **18b**, 157 (1963).
(4) R. K. Nanda and M. G. H. Wallbridge, *Inorg. Chem.*, **3**, 1798 (1964).
(5) J. M. Davidson, *Chem. Ind.* (London), 2021 (1964).
(6) F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965).
(7) F. Cariati and L. Naldini, *ibid.*, **95**, 201 (1965).
(8) N. F. Curtis, *J. Chem. Soc.*, 924 (1965).
(9) H. D. Kaesz, W. Fellman, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2753 (1965).
(10) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *J. Chem. Soc., Sect. A*, 182 (1966).
(11) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *Chem. Commun.*, 848 (1966).
(12) F. Cariati and L. Naldini, *J. Inorg. Nucl. Chem.*, **28**, 2243 (1966).
(13) S. J. Lippard and D. Ucko, unpublished work.

solution and in the solid state, and show the equivalence of all four borohydride protons in their solution nmr spectra.

As with the compounds of the main group metals, particularly aluminum, there are three possible modes of attachment of the borohydride ion to the metal atom for these complexes


I


II


III

Until recently, structure I has generally been accepted, primarily on the basis of infrared spectral evidence. X-Ray diffraction results for $Zr(BH_4)_4$ have shown, however, that structure III can also occur.[14] As part of a broad program designed to study the relationship between structure and reactivity for several transition metal borohydride complexes, we have investigated the crystal structure of $[(C_6H_5)_3P]_2Cu(BH_4)$. The results, which have been reported in a preliminary communication,[15] confirm structure I for this complex and will now be presented in detail.

Experimental Procedures and Results

Collection and Reduction of X-Ray Data.—The compound was prepared by the method of Cariati and Naldini[6] and recrystallized from chloroform–ethanol. Whereas colorless needles were commonly precipitated from such solutions, better developed crystals exhibiting several forms could be obtained by very slow growth. One such crystal of approximate dimensions 0.18 × 0.18 × 0.22 mm was obtained, mounted with hard shellac on the end of a glass fiber along the *b* axis, and used in all X-ray studies reported here. After an approximate optical alignment, the crystal was transferred to the precession camera where the space group and unit cell dimensions were determined using Zr-filtered Mo Kα radiation (λ 0.7107 A). The density was measured by flotation in an aqueous solution of potassium iodide.

Intensity data were first collected on the Weissenberg camera using molybdenum radiation and estimating the intensities visually. Although these data were sufficient for the determination of all heavy atoms in the structure, they did not appear to be accurate enough for the location of the hydrogen atoms. A second set of data was therefore collected on a Picker four-circle automated X-ray diffractometer using Cu Kα radiation (λ 1.5418 A). Fortunately, these data were sufficient for the determination of all hydrogen atoms (*vide infra*).

Since this structure represents the first one to have been carried out on our Picker diffractometer, we report here the pertinent experimental details and computational procedures used in data collection and processing. Alignment of the diffractometer was achieved using a standard beryllium acetate crystal and was subsequently checked with the borohydride crystal. Room-temperature intensity data were taken at a takeoff angle of 2.5°, a value which was found to afford sufficient intensity, resolution, and a relatively small scan range consistent with the low mosaic spread of the crystal. A symmetrically varying receiving aperture, positioned on the diffractometer dovetail track in front of the counter, was set to a 3.5 × 3.5 mm opening to minimize extraneous background. Each reflection was filtered through 0.001-in. Ni foil after diffraction from the crystal. The detector, positioned approximately 23 cm from the crystal, was a scintillation counter employing a thallium-activated sodium iodide crystal. The pulse height analyzer was adjusted to accept 95% of the peak while eliminating 78% of unwanted background. Integrated intensities were collected by the θ–2θ scan technique. The diffractometer settings were computed from the cell constants and crystal orientation matrix using Prewitt's program, CSET-4. The scan range for all reflections was 1.5° in 2θ plus an allowance for the $K\alpha_1$–$K\alpha_2$ separation which became important at high 2θ values. The scan rate was 1°/min and was symmetric with respect to the Bragg position. Each reflection was scanned once, and 10-sec background counts were taken at each end of the scan. For reflections having count rates in excess of 10,000 cps, copper foil attenuators were automatically inserted into the diffracted beam path until the intensity was reduced to less than that value. All data were displayed on the chart recorder to provide a visual check on peak shapes, printed out on paper tape as a check on the diffractometer settings, and punched on IBM cards for further processing. To monitor crystal stability and alignment, a standard reflection was measured after every 100 reflections. The integrated intensity of this standard showed no systematic variation and was always within 2% of the mean value for the entire run. For maximum efficiency, data were collected with the indices of the shortest reciprocal axes varying fastest ($h > l > k$ in this case). The resultant over-all efficiency, including the time spent recording the standard reflection, was 71%. Approximately 1800 crystallographically independent reflections within the sphere $\theta < 53°$ were collected in a period of 4.5 days.

The raw data, I, were corrected for background, use of attenuators, absorption, and Lorentz-polarization effects using a local modification (S. J. L.) of Prewitt's program, ACAC. The background correction assumes that the background for each reflection can be approximated by the average of the background readings on either side of the peak in counts per second multiplied by the time required to scan through the peak. Absorption corrections (μ = 21.5 cm^{-1}) obtained from the program were checked against an experimental measure of the change in peak intensity with ϕ for several reflections at χ = 90° and found to agree well. The data were then placed on an approximate common scale through a modification of Wilson's method.[16] From the resultant values for $|F_o|$ and $|F_o|^2$, the structure was solved by the usual Patterson, Fourier, and least-square refinement processes (see below). Scattering factor tables, appropriately corrected for anomalous dispersion ($f = f^0 + \Delta f' + i\Delta f''$) for the copper and phosphorus atoms, were obtained from the "International Tables."[17] Form factors used were for the neutral atoms. Weights were assigned to each reflection in the least-squares process according to a scheme written into Prewitt's program, ACAC, which is based on counting statistics and the direct beam stability. Of the 1800 measured reflections, only 50 had intensities less than their standard deviations. These were excluded from the refinement.

Unit Cell and Space Group.—Borohydridobis(triphenylphosphine)copper(I) crystallizes in the monoclinic system with a = 24.64 ± 0.02, b = 9.058 ± 0.006, c = 15.43 ± 0.01 A, β = 116.2 ± 0.1°. The cell volume (V = 3091 A^3) and density (ρ = 1.295 ± 0.005 g/cc) require four molecules per unit cell. The calculated density, ρ = 1.297 g/cc, agrees well with that observed. From the observed extinctions, hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$, the space group was ascertained to be Cc (No. 9) or C2/c (No. 15).[18]

Determination of the Structure.—Using the corrected data, an origin-removed, sharpened Patterson map was computed[16] and solved for the positions of the copper and phosphorus atoms. From a careful inspection of the map, we decided that the space group was probably the centrosymmetric C2/c, a choice which appears to be justified by the successful refinement of the struc-

---

(14) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 403 (1967).

(15) S. J. Lippard and K. M. Melmed, *J. Am. Chem. Soc.*, **89**, 3929 (1967).

(16) In addition to those mentioned in the text, programs for the IBM 7094 used in this work include local versions of the Zalkin Fourier program, FORDAP, the Busing–Martin–Levy structure factor calculation and least-squares refinement program, OR-FLS, the Busing–Martin–Levy error function program, OR-FFE, the Wood molecular geometry program, MGEOM, and XDATA, the Brookhaven data reduction program.

(17) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 202, 210, 214.

(18) See ref 17, Vol. I, p 101.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (×10) (IN ELECTRONS) FOR $[(C_6H_5)_3P]_2Cu(BH_4)$[a]

H	L	OBS	CAL
******K= 0******			
20	0	581	579
-18	0	428	393
-16	0	68	44
-14	0	880	876
-12	0	2098	2209
-10	0	1513	1550
-8	0	586	578
-24	2	499	442
-22	2	511	480
-20	2	927	886
-18	2	367	383
-16	2	322	267
-14	2	353	398
-12	2	1435	1478
-10	2	1684	1768
-8	2	1810	1864
6	2	505	467
8	2	1110	1106
10	2	703	717
12	2	644	651
14	2	416	391
16	2	166	127
18	2	321	316
20	2	451	437
-24	4	229	245
-22	4	958	985
-20	4	206	170
-18	4	184	222
-16	4	751	752
-14	4	726	722
-12	4	660	689
-10	4	1037	1047
-8	4	295	269
2	4	588	586
4	4	680	680
6	4	397	390
8	4	240	324
10	4	1357	1350
12	4	651	658
14	4	38	56
16	4	171	192
18	4	592	569
-24	6	352	391
-22	6	86	99
-20	6	276	282
-18	6	426	421
-16	6	821	808
-14	6	1294	1299
-12	6	250	255
-10	6	636	620
-8	6	255	247
-6	6	930	924
-4	6	720	701
-2	6	1303	1307
0	6	400	385
2	6	858	811
4	6	317	314
6	6	671	651
8	6	669	669
10	6	717	739
12	6	54	67
14	6	145	140
16	6	379	384
-24	8	101	146
-22	8	214	189
-20	8	72	85
-18	8	817	829
-16	8	866	868
-14	8	112	152
-12	8	389	388
-10	8	436	419
-8	8	83	55
-6	8	994	1004
-4	8	1626	1639
-2	8	867	831
0	8	152	172
2	8	226	209
4	8	306	317
6	8	585	608
8	8	962	970
10	8	147	155
12	8	102	13
14	8	181	159
-24	10	116	91
-22	10	59	26
-20	10	147	142
-18	10	537	558
-16	10	787	793
-14	10	365	362
-12	10	427	410
-10	10	57	28
-8	10	792	817
-6	10	1169	1171
-4	10	326	308
-2	10	75	22
2	10	369	404
4	10	1081	1119
6	10	568	579
8	10	56	68
10	10	184	196
-22	12	93	42
-20	12	403	433
-18	12	786	825
-16	12	494	510
-14	12	55	64
-12	12	236	192
-10	12	76	88
-8	12	1005	1046
-6	12	896	921
-4	12	552	569
-2	12	262	261
0	12	182	149
2	12	467	468
4	12	318	310
6	12	547	539
-20	14	319	368
-18	14	840	878
-16	14	449	495
-14	14	59	18
-12	14	94	70
-10	14	108	57
-8	14	495	519
-6	14	533	566
-4	14	353	388
-2	14	103	107
******K= 1******			
-17	15	155	157
-15	15	140	165
-13	15	94	34
-11	15	168	178
-9	15	248	257
-7	15	189	178
-5	15	171	186
-3	15	111	108
-1	14	93	141
-5	14	183	176
-7	14	366	377
-9	14	259	261
-11	14	90	119
-13	14	146	136
-17	14	332	359
-19	14	420	455
-21	13	165	142
-19	13	56	68
-17	13	151	102
-15	13	74	23
-13	13	620	645
-11	13	479	492
-9	13	323	344
-7	13	56	17
-5	13	153	133
-3	13	182	188
-1	13	189	190
1	13	396	394
3	13	348	368
5	12	305	299
3	12	216	217
1	12	152	127
-1	12	275	250
-3	12	271	284
-5	12	654	658
-7	12	699	713
-9	12	227	221
-11	12	274	268
-13	12	195	192
-15	12	407	409
-17	12	689	715
-19	12	506	528
-21	12	101	76
-23	12	138	123
-23	11	131	109
-21	11	195	210
-19	11	264	275
-17	11	250	243
-15	11	305	337
-13	11	386	395
-11	11	190	188
-9	11	64	78
-7	11	188	144
-5	11	488	484
-3	11	519	530
-1	11	547	556
1	11	167	182
3	11	257	252
5	11	87	93
7	11	378	372
9	10	114	86
7	10	383	371
5	10	680	672
3	10	447	461
1	10	88	72
-1	10	448	423
-3	10	426	432
-5	10	827	818
-7	10	955	926
-9	10	57	9
-11	10	98	66
-13	10	154	135
-15	10	376	371
-17	10	645	635
-19	10	372	369
-21	10	151	124
-23	10	94	116
-25	9	225	239
-23	9	301	291
-21	9	73	77
-19	9	170	162
-17	9	228	248
-15	9	356	349
-13	9	178	172
-11	9	712	698
-9	9	308	310
-7	9	492	492
-5	9	78	20
-3	9	398	377
-1	9	441	412
1	9	338	315
3	9	394	376
5	9	114	95
7	9	150	122
9	9	506	488
11	9	104	118
13	8	77	41
11	8	197	168
9	8	241	232
7	8	759	764
5	8	476	486
3	8	334	298
1	8	189	186
-1	8	84	11
-3	8	1012	1040
-5	8	731	748
-7	8	494	472
-9	8	63	32
-11	8	213	168
-13	8	296	290
-15	8	553	578
-17	8	764	775
-21	8	65	28
-25	8	179	179
-25	7	247	238
-23	7	440	427
-21	7	147	101
-19	7	126	134
-17	7	278	285
-15	7	531	513
-13	7	756	737
-11	7	715	683
-9	7	289	278
-7	7	47	20
-5	7	816	792
-3	7	974	968
-1	7	45	53
1	7	837	806
3	7	191	182
5	7	260	253
7	7	238	242
9	7	410	392
11	7	141	158
13	7	186	157
15	7	152	121
15	6	83	2
13	6	144	111
11	6	229	225
9	6	852	845
7	6	462	467
5	6	68	90
3	6	349	344
1	6	360	363
-1	6	1438	1397
-3	6	1040	991
-5	6	432	412
-7	6	141	130
-9	6	88	82
-11	6	295	292
-13	6	590	600
-15	6	935	937
-17	6	545	570
-19	6	284	289
-21	6	63	14
-23	6	161	139
-25	6	482	481
-25	5	49	35
-23	5	93	86
-21	5	580	573
-19	5	172	147
-17	5	374	377
-15	5	368	332
-13	5	63	29
-11	5	94	43
-9	5	1148	1100
-7	5	585	579
-5	5	994	972
-3	5	1186	1174
-1	5	412	380
1	5	389	396
3	5	315	309
5	5	732	719
7	5	635	608
9	5	475	478
11	5	337	301
13	5	88	94
15	5	133	141
17	5	167	126
19	4	488	489
17	4	98	84
15	4	181	170
13	4	67	70
11	4	603	575
9	4	829	823
7	4	422	382
3	4	62	18
1	4	91	14
-7	4	194	217
-9	4	194	185
-11	4	785	752
-13	4	785	788
-15	4	817	831
-19	4	328	317
-21	4	373	379
-23	4	385	366
-23	3	86	43
-21	3	49	42
-19	3	407	384
-17	3	713	687
15	3	854	808
-13	3	1145	1128
-11	3	65	65
-9	3	108	61
3	3	1360	1444
5	3	123	162
7	3	430	440
9	3	459	442
11	3	573	551
13	3	78	40
15	3	298	227
17	3	442	432
19	3	320	308
21	2	390	392
19	2	376	359
17	2	195	193
15	2	76	48
13	2	322	319
11	2	819	822
9	2	834	859
7	2	418	419
5	2	191	139
-9	2	708	714
-11	2	864	873
-13	2	1098	1074
-15	2	338	339
-17	2	494	492
-19	2	151	119
-21	2	470	459
-23	2	369	351
-23	1	102	109
-21	1	289	330
-19	1	554	533
-17	1	361	272
-15	1	648	573
-13	1	77	28
-11	1	579	582
-9	1	331	297
7	1	1691	1768
9	1	70	77
11	1	435	440
13	1	354	341
15	1	261	265
17	1	138	89
19	1	560	510
21	1	63	60
21	0	330	310
19	0	143	142
17	0	163	143
15	0	119	116
13	0	578	590
11	0	1226	1240
9	0	616	633
7	0	193	175
******K= 2******			
6	0	167	101
8	0	83	72
10	0	806	797
12	0	216	124
14	0	53	2
16	0	300	255
18	0	100	23
20	0	96	26
22	0	356	321
20	1	371	407
18	1	446	451
16	1	254	221
14	1	219	226
12	1	798	780
10	1	281	290
8	1	356	375
6	1	1061	1122
-6	1	643	645
-8	1	1002	1018
-10	1	271	284
-12	1	264	265
-14	1	697	692
-16	1	472	455
-18	1	94	113
-20	1	400	401
-22	1	214	224
-22	2	325	293
-20	2	202	132
-18	2	490	469
-16	2	214	191
-14	2	472	494
-12	2	746	750
-10	2	619	623
-8	2	1257	1253
-6	2	609	605
4	2	532	583
6	2	574	580
8	2	99	44
10	2	638	645
12	2	122	121
14	2	95	37
16	2	276	289
18	2	106	96
20	2	324	323
18	3	304	314
16	3	360	382
14	3	308	307
12	3	297	320
10	3	663	632
8	3	268	270
6	3	549	542
4	3	948	933
2	3	50	39
-6	3	731	735
-8	3	1141	1120
-10	3	245	287
-12	3	470	461
-14	3	625	612
-16	3	530	539
-18	3	393	365
-20	3	296	299
-22	3	93	18
-24	3	231	234
-24	4	380	343
-22	4	188	163
-20	4	189	155
-18	4	286	271
-16	4	162	147
-14	4	535	531
-12	4	489	522
-10	4	649	618
-8	4	621	621
-6	4	496	433
-4	4	1288	1284
-2	4	335	275
0	4	400	394
2	4	901	908
4	4	417	436
6	4	385	345
8	4	980	955
10	4	117	89
12	4	172	133
14	4	391	368
16	4	160	161
18	4	160	151
16	5	143	149
14	5	336	331
12	5	108	101
10	5	450	425
8	5	702	676
6	5	543	553
4	5	699	747
2	5	64	35
0	5	142	160
-2	5	1259	1226
-4	5	1163	1107
-6	5	672	628
-8	5	246	215
-10	5	966	937
-12	5	260	261
-14	5	336	343
-16	5	688	689
-18	5	146	164
-20	5	495	491
-22	5	289	294
-24	5	42	40
-24	6	196	155
-22	6	87	70
-20	6	235	229
-18	6	310	271
-16	6	691	660
-14	6	395	366
-12	6	290	257
-10	6	912	873
-8	6	487	452
-6	6	235	213
-4	6	984	921
-2	6	1480	1421
0	6	248	219
2	6	1288	1300
4	6	207	228
6	6	76	34
8	6	847	831
10	6	351	324
12	6	191	140
14	6	417	391
16	6	150	163
14	7	137	147
12	7	342	357
10	7	386	366
8	7	179	152
6	7	390	382
4	7	596	583
2	7	725	718
0	7	68	38
-2	7	928	919
-4	7	295	263
-6	7	797	773
-8	7	362	391
-10	7	556	566
-12	7	665	640
-14	7	489	448
-16	7	467	442
-18	7	304	287
-20	7	80	36
-22	7	585	620
-24	7	211	199
-24	8	96	20
-22	8	225	198
-20	8	432	420
-18	8	266	244
-16	8	651	639
-14	8	715	669
-12	8	139	75
-10	8	434	444
-8	8	345	340
-6	8	107	143
-4	8	292	254
-2	8	505	504
0	8	192	224
2	8	283	311
4	8	156	132
6	8	460	440
8	8	83	91
10	8	82	100
12	8	226	204
10	9	419	439
8	9	513	533
6	9	70	37
4	9	90	37
2	9	702	676
0	9	289	284
-2	9	908	888
-4	9	445	425
-6	9	278	274
-8	9	333	315
-10	9	399	375
-12	9	477	446
-14	9	560	565
-16	9	391	396
-18	9	455	488
-20	9	63	22
-22	9	302	302
-24	9	241	248
-24	10	69	28
-22	10	104	105
-20	10	219	206
-18	10	389	393
-16	10	246	249
-14	10	61	56
-12	10	218	222
-10	10	285	311
-8	10	71	7
-6	10	435	400
-4	10	599	592
0	10	612	606
2	10	95	9
4	10	111	15
6	10	296	282
8	10	319	301
10	10	114	57
8	11	147	164
6	11	194	200
4	11	115	128
2	11	360	388
0	11	590	609
-2	11	257	287
-4	11	433	424
-6	11	118	89
-8	11	161	145
-10	11	644	657
-12	11	628	648
-14	11	168	160
-16	11	161	153
-18	11	382	367
-20	11	233	248
-22	11	263	266
-22	12	164	149
-20	12	71	34
-18	12	423	425
-16	12	305	314
-14	12	158	172
-12	12	306	299
-10	12	137	103
-8	12	200	194
-6	12	381	384
-4	12	135	120
-2	12	176	184
0	12	211	205
4	12	276	260
2	13	291	306
0	13	221	221
-2	13	67	53
-4	13	214	221
-6	13	219	239
-8	13	520	551
-10	13	223	230
-12	13	503	502
-14	13	272	281
-18	13	94	90
-20	13	363	386
-18	14	139	145
-16	14	181	148
-14	14	90	61
-10	14	143	106
-8	14	300	272
-4	14	133	137
-2	14	229	202
0	14	128	109
-6	15	319	358
-8	15	279	285
-10	15	87	96
-12	15	93	137
-14	15	134	142
-16	15	281	323
******K= 3******			
-13	15	195	211
-11	15	89	110
-9	15	223	263
-3	14	232	224
-5	14	50	45
-7	14	130	114
-9	14	180	147
-11	14	303	325
-13	14	489	523
-15	14	153	167
-19	13	258	271
-17	13	102	58
-15	13	231	252
-13	13	373	395
-11	13	162	186
-9	13	139	152
-7	13	268	288
-5	13	254	279
-3	13	236	229
-1	13	118	123
1	13	250	242
3	12	172	150
1	12	312	305
-1	12	357	355
-3	12	410	426
-5	12	66	61
-7	12	179	165
-9	12	99	39
-11	12	331	319
-13	12	292	284
-15	12	416	430
-17	12	128	94
-19	12	65	25
-21	12	61	38
-21	11	84	53
-19	11	208	213
-17	11	386	395
-15	11	56	15
-13	11	334	341
-11	11	704	721
-9	11	241	235
-7	11	157	134
-5	11	178	147
-3	11	388	422
-1	11	214	209
1	11	457	480
3	11	279	287
5	11	40	47
7	11	144	153
9	10	258	241
7	10	232	229
5	10	74	61
3	10	155	170
1	10	632	623
-1	10	257	247
-3	10	128	126
-5	10	152	159
-7	10	68	40
-9	10	208	209
-11	10	825	831
-13	10	371	353
-15	10	67	50
-17	10	293	292
-19	10	192	198
-21	10	192	212
-23	10	477	480
-23	9	174	184
-21	9	208	208
-19	9	221	230
-17	9	537	512
-15	9	352	347
-13	9	193	191
-11	9	123	143
-9	9	503	501
-7	9	483	457
-5	9	508	466
-3	9	661	614
-1	9	138	149
1	9	348	326
3	9	392	380
5	9	103	55
7	9	345	344
9	9	397	398
11	9	142	156
11	8	212	198
9	8	74	9
7	8	74	40
5	8	81	47
3	8	401	381
1	8	499	514
-1	8	88	107
-3	8	175	167
-5	8	90	61
-7	8	444	413
-9	8	771	740
-11	8	430	407
-13	8	76	96
-15	8	302	299
-17	8	151	151
-19	8	435	468
-21	8	499	507
-23	8	165	187
-23	7	244	257
-21	7	572	563
-19	7	182	125
-17	7	368	369
-15	7	214	211
-13	7	172	162
-11	7	456	418
-9	7	855	865
-7	7	874	871
-5	7	365	344
-3	7	93	96
-1	7	593	575
1	7	104	67
3	7	822	816
5	7	648	622
7	7	41	14
9	7	146	164
11	7	452	457
13	7	173	218
15	6	347	337
13	6	318	314
11	6	366	380
9	6	137	111
7	6	346	351
5	6	159	162
3	6	1042	1013
1	6	583	571
-1	6	460	442
-3	6	566	545
-5	6	209	214
-7	6	354	311
-9	6	1392	1384
-11	6	363	380
-13	6	209	180
-15	6	232	226
-17	6	234	228
-19	6	399	352
-21	6	460	460
-23	6	54	59
-23	5	187	188
-21	5	323	328
-19	5	171	176
-17	5	136	102
-15	5	322	321
-13	5	715	693
-11	5	877	860
-9	5	679	640
-7	5	156	132
-5	5	112	99
-3	5	869	824
-1	5	980	931
1	5	599	567
3	5	847	851
5	5	203	210
7	5	388	376
9	5	166	143
11	5	196	187
13	5	463	466
15	5	283	268
17	5	208	224
17	4	136	148
15	4	577	583
13	4	410	413
11	4	87	66
9	4	512	513
7	4	149	140
5	4	765	754
3	4	1122	1180
1	4	569	576
-1	4	277	252
-3	4	1105	1074
-5	4	709	715
-7	4	807	808
-9	4	853	852
-11	4	197	174
-13	4	151	138
-15	4	72	73
-17	4	372	384
-19	4	367	396
-21	4	356	360
-23	4	69	24
-23	3	81	24
-21	3	182	168
-19	3	445	426
-17	3	388	393
-15	3	494	485
-13	3	233	241
-11	3	565	557
-9	3	233	217
-7	3	1117	1076
-5	3	654	662
-3	3	131	146
-1	3	1413	1443
1	3	996	1006
3	3	35	25
5	3	473	458
7	3	310	316
9	3	619	617
11	3	437	437
13	3	406	380
15	3	241	229
17	3	140	122
19	3	205	227
19	2	66	17
17	2	249	242
15	2	381	380
13	2	272	265
11	2	85	63
9	2	325	331
7	2	668	711
5	2	766	793
3	2	227	237
1	2	200	219
-1	2	467	499
-3	2	966	945
-5	2	366	367
-7	2	1166	1161
-9	2	602	596
-11	2	782	742
-13	2	142	124
-15	2	178	169
-17	2	410	411
-19	2	635	623
-21	2	114	85
-21	1	252	251
-19	1	146	109
-17	1	405	380
-15	1	783	748
-13	1	185	202
-11	1	237	255
-9	1	57	88
-7	1	603	581
-5	1	1430	1445
-3	1	1189	1204
-1	1	719	691
1	1	57	31
3	1	331	324
5	1	705	699
7	1	446	434
9	1	922	930
11	1	368	371
13	1	314	371
15	1	98	132
17	1	148	133
19	1	451	462
21	0	181	147
19	0	111	128
17	0	723	737
15	0	402	416
13	0	113	93
11	0	197	210
9	0	203	218
7	0	920	919
5	0	992	1002
3	0	418	435
1	0	334	311
******K= 4******			
0	0	829	803
2	0	476	477
4	0	926	956
6	0	924	988
8	0	482	509
0	0	246	237
12	0	145	96
14	0	411	581
16	0	778	814
18	0	514	506
20	0	81	66
20	1	104	105
16	1	99	98
14	1	346	350
12	1	105	27
10	1	171	206
8	1	335	339
6	1	133	112
4	1	385	316
2	1	209	237
0	1	334	339
-2	1	52	42
-4	1	379	393
-6	1	952	949
-8	1	84	70
-10	1	119	95
-12	1	82	70
-14	1	159	120
-16	1	308	274
-18	1	222	165
-20	1	157	160
-20	2	596	579
-18	2	487	480
-16	2	274	282
-14	2	78	49
-12	2	323	281
-10	2	763	743
-8	2	1265	1274
-6	2	1041	1036
-4	2	208	210
-2	2	163	169
0	2	296	302
2	2	646	654
4	2	1513	1594
6	2	863	868
8	2	312	326
10	2	236	220
12	2	202	216
14	2	817	831
16	2	387	952
18	2	188	167
18	3	163	167
16	3	87	40
14	3	95	39
12	3	48	10
10	3	287	281
8	3	166	158
6	3	242	236
4	3	293	316
2	3	229	180
0	3	87	35
-2	3	463	446
-4	3	256	240
-6	3	512	446
-8	3	126	142
-10	3	360	336
-12	3	145	121
-14	3	138	108
-16	3	366	363
-18	3	82	23
-20	3	99	87
-22	3	43	31
-22	4	236	252
-20	4	569	547
-18	4	730	726
-16	4	400	455
-14	4	54	13
-12	4	96	56
-10	4	239	243
-8	4	1267	1265
-6	4	1469	1459
-4	4	588	579
-2	4	414	452
0	4	316	289
2	4	1151	1192
4	4	1021	1074
6	4	801	811
8	4	76	104
10	4	230	210
12	4	666	650
14	4	567	572
16	4	390	376
14	5	216	216
12	5	183	203
10	5	192	194
8	5	91	85
6	5	125	133
4	5	411	404
2	5	535	534
0	5	39	43
-2	5	245	243
-4	5	459	466
-6	5	37	37
-8	5	471	455
-10	5	203	224
-12	5	309	309
-14	5	95	105
-20	5	109	62
-22	5	175	171
-22	6	321	342
-20	6	552	530
-18	6	511	542
-16	6	188	161
-14	6	99	86
-12	6	169	160
-10	6	863	838
-8	6	1452	1453
-6	6	376	338
-4	6	167	188
-2	6	640	604
0	6	489	495
2	6	850	854
4	6	796	803
6	6	153	182
8	6	38	28
10	6	473	467
12	6	330	341
14	6	359	333
12	7	53	23
10	7	185	174
8	7	312	338
6	7	72	31
4	7	192	176
2	7	166	131
0	7	57	36
-2	7	143	129
-4	7	468	457
-6	7	368	365
-8	7	32	30
-10	7	223	211
-12	7	185	176
-14	7	113	62
-16	7	267	282
-18	7	89	146
-20	7	114	108
-22	8	502	524
-20	8	552	566
-18	8	235	235
-16	8	125	106
-14	8	125	109
-12	8	340	322
-10	8	1206	1222
-8	8	519	500
-6	8	102	98
-4	8	225	202
-2	8	463	456
0	8	642	632
2	8	688	677
4	8	355	368
6	8	197	201
8	8	120	42
10	8	308	313
8	9	152	120
4	9	79	95
2	9	96	128
0	9	108	142
-2	9	86	79
-4	9	223	218
-6	9	101	98
-8	9	278	266
-10	9	102	142
-12	9	94	92
-14	9	53	74
-16	9	232	220
-18	9	53	40
-20	9	111	130
-22	9	86	75
-22	10	514	530
-20	10	187	204
-18	10	144	159
-16	10	122	79
-14	10	309	300
-12	10	865	870
-10	10	667	683
-8	10	119	101
-6	10	104	74
-4	10	196	197
-2	10	476	489
0	10	524	520
2	10	630	646
4	10	174	195
6	10	171	150
4	11	101	95
2	11	122	121
0	11	142	112
-2	11	272	313
-10	11	76	23
-12	11	344	368
-14	11	189	207
-16	11	64	15
-20	11	112	86
-20	12	137	124
-18	12	107	113
-16	12	158	190
-14	12	222	236
-12	12	445	482
-10	12	437	457
-8	12	164	208
-6	12	114	152
-4	12	286	297
-2	12	265	265
0	12	426	422
2	12	280	311
0	13	77	67
-2	13	102	87
-4	13	69	83
-6	13	78	48
-8	13	69	72
-10	13	130	160
-12	13	57	93
-14	13	148	145
-16	13	75	55
-18	13	136	139
-14	14	442	475
-12	14	487	327
-10	14	96	25
-8	14	99	28
-6	14	83	97
******K= 5******			
-13	13	186	199
-11	13	127	150
-9	13	58	23
-7	13	133	143
-5	13	69	77
-1	12	336	361
-3	12	143	179
-5	12	172	198
-7	12	110	89
-9	12	178	176
-11	12	369	412
-13	12	384	420
-15	12	126	104
-17	12	73	98
-19	11	208	202
-17	11	229	254
-15	11	104	64
-13	11	123	106
-11	11	313	311
-9	11	65	11
-7	11	173	163
-5	11	275	298
-3	11	174	177
-1	11	87	94
1	11	129	129
3	11	100	66
5	10	64	33
3	10	377	392
1	10	318	310
-1	10	299	300
-3	10	226	241
-5	10	147	174
-7	10	224	277
-9	10	402	426
-11	10	266	258
-13	10	373	380
-15	10	65	22
-17	10	118	157
-19	10	229	268
-19	9	101	56
-17	9	102	28
-15	9	297	312
-11	9	214	210
-9	9	319	324
-7	9	147	153
-5	9	207	208
-3	9	139	133
-1	9	107	38
1	9	195	155
3	9	209	205
5	9	228	238
7	9	75	79
9	8	70	70
7	8	185	153
5	8	132	126
3	8	635	662
1	8	796	809
-1	8	280	275
-3	8	86	20
-5	8	162	110
-7	8	31	53
-9	8	945	948
-11	8	1041	1053
-13	8	46	22
-15	8	250	214
-17	8	65	49
-19	8	331	342
-21	8	498	513
-21	7	95	28
-19	7	74	52
-17	7	112	95
-15	7	412	443
-13	7	323	331
-11	7	118	88
-9	7	246	201
-7	7	94	46
-5	7	200	201
-3	7	287	277
-1	7	413	444
1	7	317	314
3	7	110	66
5	7	315	307
7	7	153	137
9	7	128	82
11	7	341	333
13	6	435	424
11	6	130	145
9	6	153	136
7	6	235	209
5	6	366	381
3	6	948	977
1	6	700	718
-1	6	191	194
-3	6	217	230
-5	6	244	237
-7	6	1115	1132
-9	6	937	961
-11	6	478	486
-13	6	150	128
-15	6	168	151
-17	6	287	310
-19	6	545	564
-21	6	407	417
-21	5	97	94
-19	5	158	192
-17	5	137	99
-15	5	160	115
-13	5	426	401
-11	5	68	56
-9	5	340	318
-7	5	197	178
-5	5	402	412
-3	5	677	699
-1	5	163	145
1	5	40	18
3	5	63	43
5	5	145	153
7	5	608	600
9	5	216	196
11	5	214	215
15	4	222	200
13	4	569	581
11	4	561	568
9	4	224	196
7	4	106	92
5	4	627	649
3	4	828	853
1	4	604	616
-1	4	269	273
-3	4	128	108
-5	4	334	291
-7	4	798	765
-9	4	859	855
-11	4	181	168
-13	4	158	98
-15	4	230	256
-17	4	377	380
-19	4	431	390
-21	4	468	465
-19	3	96	40
-17	3	269	281
-15	3	108	62
-13	3	486	470
-11	3	296	284
-9	3	161	150
-7	3	276	274
-5	3	158	134
-3	3	53	16
-1	3	643	587
1	3	513	487
3	3	305	323
5	3	57	45
7	3	437	447
9	3	131	96
11	3	257	236
13	3	93	62
15	3	140	117
17	2	299	310
15	2	751	765
13	2	373	389
11	2	129	117
9	2	164	145
7	2	354	378
5	2	1053	1072
3	2	1116	1129
1	2	112	70
-1	2	301	267
-3	2	113	89
-5	2	645	661
-7	2	737	736
-9	2	719	692
-11	2	338	298
-13	2	55	28
-15	2	188	197
-17	2	385	371
-19	2	441	420
-17	1	235	221
-15	1	279	244
-13	1	164	144
-11	1	144	173
-9	1	123	152
-7	1	163	158
-5	1	679	642
-3	1	584	558
-1	1	270	285
1	1	55	17
3	1	309	319
5	1	51	47
7	1	420	412
9	1	463	424
11	1	277	224
13	1	186	177
15	1	79	57
17	1	102	97
19	0	400	389
17	0	413	412
15	0	311	327
13	0	250	227
11	0	78	9
9	0	299	264
7	0	990	999
5	0	651	684
3	0	68	84
1	0	566	541
******K= 6******			
0	0	325	335
2	0	130	124
4	0	179	166
6	0	871	865
8	0	268	277
10	0	197	164
12	0	255	240
14	0	105	81
18	0	194	170
16	1	101	71
14	1	312	323
12	1	507	492
10	1	40	55
8	1	443	422
6	1	267	266
4	1	329	319
2	1	535	550
0	1	476	473
-2	1	207	188
-4	1	550	492
-6	1	583	552
-8	1	433	442
-10	1	92	50
-12	1	378	379
-14	1	300	311
-16	1	314	303
-18	1	160	149
-18	2	304	287
-16	2	227	214
-14	2	102	115
-12	2	312	295
-10	2	96	71
-8	2	425	417
-6	2	452	444
-4	2	84	47
-2	2	87	103
0	2	76	82
2	2	198	183
4	2	618	601
6	2	495	481
8	2	397	398
10	2	289	262
12	2	92	6
14	2	383	386
16	2	378	368
14	3	166	158
12	3	42	15
10	3	477	484
8	3	317	311
6	3	736	789
4	3	349	353
2	3	100	65
0	3	275	244
-2	3	530	478
-4	3	510	482
-6	3	411	421
-8	3	466	475
-10	3	294	280
-12	3	131	94
-14	3	373	339
-16	3	356	366
-18	3	191	206
-18	4	182	169
-16	4	139	168
-14	4	276	254
-12	4	298	297
-10	4	358	353
-8	4	688	672
-6	4	407	399
-4	4	99	104
-2	4	414	404
0	4	121	102
2	4	178	209
4	4	832	838
6	4	141	142
8	4	215	190
10	4	106	60
12	4	69	22
12	5	64	142
10	5	213	210
8	5	329	332
6	5	554	568
4	5	219	204
2	5	134	94
-2	5	712	725
-4	5	562	573
-6	5	229	207
-8	5	310	309
-10	5	270	265
-12	5	151	129
-14	5	521	519
-16	5	242	232
-18	5	144	173
-18	6	267	261
-16	6	174	194
-14	6	408	401
-12	6	131	109
-10	6	260	273
-8	6	467	438
-6	6	276	268
-4	6	100	39
-2	6	83	66
0	6	138	118
2	6	334	323
4	6	292	292
6	6	300	270
10	6	61	23
8	7	320	340
6	7	141	160
4	7	134	135
2	7	56	21
0	7	262	26[illegible]
-2	7	563	591
-4	7	746	761
-6	7	441	49[illegible]
-8	7	306	33[illegible]
-10	7	94	6[illegible]
-12	7	442	44[illegible]
-14	7	558	55[illegible]
-16	7	487	49[illegible]
-18	7	177	18[illegible]
-18	8	81	1[illegible]
-16	8	208	18[illegible]
-14	8	124	12[illegible]
-12	8	596	62[illegible]
-10	8	476	47[illegible]
-8	8	116	12[illegible]
-6	8	353	32[illegible]
-4	8	375	351
-2	8	107	10[illegible]
0	8	464	44[illegible]
2	8	596	550
4	8	95	56
6	8	300	256
4	9	132	164
2	9	308	324
0	9	260	280
-2	9	250	249
-4	9	356	362
-6	9	55	29
-8	9	314	316
-10	9	406	447
-12	9	171	210
-14	9	307	317
-16	9	248	261
-18	9	98	94
-16	10	289	263
-14	10	101	17
-12	10	246	248
-10	10	311	279
-8	10	256	249
-6	10	127	78
-4	10	92	66
-2	10	78	91
0	10	218	203
2	10	229	218
0	11	312	339
-2	11	234	270
-4	11	155	175
-6	11	176	209
-8	11	91	88
-10	11	259	279
-12	11	400	427
-14	11	193	188
-12	12	290	275
-10	12	141	115
-8	12	129	90
-6	12	187	163
******K= 7******			
-3	10	143	95
-5	10	363	384
-7	10	322	332
-9	10	99	61
-11	10	364	366
-13	9	140	162
-11	9	147	133
-9	9	224	223
-7	9	214	242
-5	9	361	358
-3	9	285	283
-1	9	168	196
1	9	242	258
3	8	72	33
1	8	142	99
-1	8	234	229
-3	8	254	242
-5	8	436	423
-7	8	108	64
-9	8	80	24
-11	8	92	50
-13	8	169	140
-15	8	235	229
-15	7	176	201
-13	7	252	257
-11	7	249	293
-9	7	218	210
-7	7	317	302
-5	7	484	515
-3	7	274	278
-1	7	145	153
1	7	79	83
3	7	342	351
5	7	280	303
7	6	182	182
5	6	214	210
3	6	76	46
1	6	105	77
-1	6	87	16
-3	6	66	62
-5	6	170	113
-7	6	229	236
-9	6	36	26
-11	6	77	15
-13	6	176	162
-15	6	118	102
-17	5	128	127
-15	5	390	409
-13	5	405	380
-11	5	441	449
-9	5	372	367
-7	5	201	184
-5	5	103	91
-3	5	596	624
-1	5	533	550
1	5	326	325
3	5	343	330
5	5	157	193
7	5	150	106
9	5	230	244
11	4	500	489
9	4	156	126
7	4	70	53
5	4	288	258
3	4	275	250
1	4	328	315
-1	4	605	581
-3	4	409	364
-5	4	130	127
-7	4	588	581
-9	4	122	92
-11	4	180	174
-13	4	470	458
-15	4	215	209
-17	4	176	153
-15	3	359	350
-13	3	236	217
-11	3	124	108
-9	3	322	344
-7	3	485	528
-5	3	244	251
-3	3	540	526
-1	3	553	518
1	3	157	120
3	3	93	97
5	3	437	474
7	3	298	334
9	3	505	518
11	3	369	360
13	2	73	30
11	2	444	439
9	2	260	238
7	2	91	33
3	2	72	69
1	2	237	246
-1	2	544	537
-3	2	363	311
-5	2	203	205
-7	2	459	460
-9	2	124	138
-11	2	320	301
-13	2	483	464
-15	2	62	58
-15	1	315	348
-13	1	421	433
-11	1	218	207
-9	1	121	133
-7	1	509	510
-5	1	271	250
-3	1	338	325
-1	1	396	382
1	1	488	511
3	1	250	265
5	1	371	402
7	1	358	336
9	1	147	114
11	1	360	360
13	1	330	355
15	0	289	271
13	0	260	292
11	0	455	438
9	0	186	168
7	0	97	64
5	0	569	595
3	0	72	21
1	0	560	577
******K= 8******			
0	0	701	704
2	0	424	408
4	0	161	147
6	0	176	181
8	0	293	329
10	0	443	448
12	0	456	458
10	1	328	320
8	1	75	46
6	1	134	126
4	1	97	110
2	1	145	163
0	1	319	356
-2	1	299	295
-4	1	100	55
-6	1	132	102
-8	1	83	19
-10	1	301	324
-12	1	163	171
-12	2	585	582
-10	2	288	281
-8	2	181	171
-6	2	258	245
-4	2	94	66
-2	2	810	826
0	2	671	686
2	2	213	230
4	2	92	16
6	2	102	58
8	2	128	125
10	2	397	404
8	3	175	165
6	3	84	57
4	3	82	77
2	3	222	262
0	3	402	394
-2	3	318	292
-4	3	170	134
-6	3	96	124
-8	3	197	238
-10	3	166	182
-12	3	258	264
-12	4	367	365
-10	4	175	192
-8	4	120	142
-6	4	46	7
-4	4	514	487
-2	4	444	414
0	4	308	329
2	4	145	167
4	4	137	139
6	4	197	218
6	5	90	113
4	5	147	181
2	5	156	123
0	5	184	195
-2	5	175	173
-4	5	211	237
-6	5	65	9
-8	5	149	137
-10	5	205	190
-12	5	253	246
-12	6	89	54
-10	6	95	74
-8	6	225	228
-6	6	261	257
-4	6	555	570
-2	6	411	409
0	6	71	39
2	6	79	12
4	6	146	151
-2	7	61	39
-4	7	167	163
-6	7	131	130
-8	7	357	358
-10	7	124	134
-8	8	145	84
-6	8	310	300
-4	8	499	503
-2	8	237	230
******K= 9******			
-1	4	336	346
-3	4	488	508
-5	4	279	280
-7	3	264	292
-5	3	114	116
-3	3	101	77
-1	3	94	16
1	3	93	54
3	3	105	58
3	2	62	49
1	2	234	242
-1	2	617	615
-3	2	533	555
-5	2	30	6
-7	2	38	36
-7	1	201	199
-5	1	109	118
-3	1	115	111
-1	1	109	62
1	1	55	7
3	1	107	83
5	1	185	180
5	0	103	132
3	0	129	131
1	0	422	429

---

[a] The calculated value of $F(000)$ is 12,330.

TABLE II

FINAL POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR $[(C_6H_5)_3P]_2Cu(BH_4)$[a,b]

Atom	x	y	z	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.0	0.1149 (1)	0.25	14.3 (2)	74 (1)	362 (6)	0.0	10.4 (3)	0.0
P	0.08998 (5)	−0.0045 (1)	0.29861 (9)	14.3 (3)	89 (2)	45.8 (8)	−2.1 (6)	11.7 (4)	−1 (1)
B	0.0	0.356 (1)	0.25	38 (3)	60 (10)	110 (8)	0.0	20 (4)	0.0
CA1	0.1539 (2)	0.1137 (5)	0.3188 (3)	14 (1)	103 (7)	49 (3)	4 (3)	9 (2)	−7 (4)
CA2	0.2032 (2)	0.0668 (6)	0.3039 (4)	15 (1)	160 (10)	63 (4)	−11 (3)	13 (2)	−6 (5)
CA3	0.2524 (2)	0.1597 (8)	0.3259 (4)	19 (1)	250 (10)	71 (4)	−3 (4)	18 (2)	24 (6)
CA4	0.2531 (3)	0.2984 (7)	0.3636 (4)	28 (2)	200 (10)	77 (5)	29 (4)	15 (2)	−12 (6)
CA5	0.2045 (3)	0.3450 (7)	0.3778 (5)	24 (2)	160 (10)	108 (5)	18 (3)	19 (2)	−2 (6)
CA6	0.1561 (2)	0.2526 (6)	0.3567 (4)	19 (1)	118 (8)	81 (4)	−14 (3)	16 (2)	−17 (5)
CB1	0.3836 (2)	0.3843 (5)	0.0914 (3)	13 (1)	89 (7)	41 (3)	2 (2)	9 (2)	−1 (4)
CB2	0.4246 (2)	0.3058 (6)	0.0725 (4)	16 (1)	127 (8)	71 (4)	−1 (3)	14 (2)	−14 (5)
CB3	0.4078 (2)	0.2190 (6)	−0.0095 (4)	22 (1)	140 (9)	64 (4)	−16 (3)	14 (2)	−35 (5)
CB4	0.3495 (3)	0.2126 (6)	−0.0732 (4)	30 (2)	136 (9)	59 (4)	−3 (3)	20 (2)	−18 (5)
CB5	0.3053 (3)	0.2903 (7)	−0.0591 (4)	24 (2)	190 (10)	60 (4)	1 (3)	9 (2)	−18 (5)
CB6	0.3235 (2)	0.3756 (6)	0.0260 (4)	22 (1)	154 (9)	55 (4)	3 (3)	12 (2)	−17 (5)
CC1	0.4122 (2)	0.3660 (5)	0.2928 (3)	18 (1)	83 (7)	47 (3)	1 (2)	13 (2)	9 (4)
CC2	0.4229 (2)	0.4270 (6)	0.3837 (4)	26 (1)	152 (9)	53 (4)	12 (3)	19 (2)	1 (5)
CC3	0.4298 (2)	0.3296 (6)	0.4600 (4)	29 (2)	170 (10)	50 (4)	13 (3)	20 (2)	11 (5)
CC4	0.4275 (2)	0.1800 (6)	0.4460 (4)	32 (2)	149 (9)	65 (4)	−1 (3)	27 (2)	18 (5)
CC5	0.4178 (3)	0.1213 (7)	0.3579 (4)	38 (2)	117 (9)	68 (4)	−1 (3)	26 (2)	15 (5)
CC6	0.4107 (2)	0.2153 (5)	0.2822 (4)	30 (2)	101 (8)	49 (4)	−7 (3)	17 (2)	−2 (5)
H_b	0.018 (2)	0.299 (6)	0.193 (3)	5.3 (1.5)[d]					
H_t	0.053 (2)	0.430 (6)	0.303 (4)	5.4 (1.4)					

[a] See Figure 1 for atom-labeling scheme. [b] Standard deviations, in parentheses beside each entry, occur in the last significant figure for each parameter. [c] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Values reported are $\times 10^4$. [d] $\beta_{11} = B$, A^2, since hydrogen atoms were only refined isotropically.

ture. In C2/c, the molecule is required to have a twofold symmetry axis with the copper and boron atoms on the special positions (4e): $\pm(0, y, {}^1/_4)$; $\pm({}^1/_2, {}^1/_2 + y, {}^1/_4)$, and the remaining atoms on the general eightfold positions (8f): $\pm(x, y, z)$; $\pm({}^1/_2 + x, {}^1/_2 + y, z)$; $\pm(x, \bar{y}, {}^1/_2 + z)$; $\pm({}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$.[18]

After a cycle of least-squares refinement of the over-all scale factor and heavy-atom positional parameters, the latter were used to determine the signs of the structure factors for a difference Fourier synthesis. The Fourier map revealed the locations of the 19 remaining nonhydrogen atoms in the asymmetric unit. Four cycles of least-squares refinement of the scale factor, atomic positional parameters, and isotropic thermal parameters converged to values of 0.094 and 0.077 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 stage revealed several possible hydrogen atom peaks as well as anisotropic thermal motion for the other atoms. Additional refinement was therefore carried out in which all atoms were assigned anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. This led to values of $R_1 = 0.077$ and $R_2 = 0.062$ for the discrepancy indices. A difference Fourier map was then prepared from which all 17 crystallographically independent hydrogen atoms were located. The peak heights for these atoms ranged from 0.606 to 0.350 e/A^3 on a scale where the average value for a carbon atom was 2.250 e/A^3. No other major peaks (>0.350 e/A^3) appeared on this Fourier, indicating the probable correctness of the structure. Least-squares refinement of all atoms, with isotropic hydrogen atom thermal parameters and anisotropic thermal parameters for all other atoms, converged to final values of 0.059 and 0.044 for R_1 and R_2.

Hamilton's test[19] was carried out to discover whether the reduction of R_2 from 0.062 to 0.044 on addition of hydrogen atoms resulted merely from an increase in the number of parameters. The ratio of weighted R factors is 1.41; if it were only 1.29 the probability that the extra parameters were meaningless would be 0.005. Thus, assuming there are only random errors in the data, the hydrogen atoms appear to be statistically significant at the 0.5% confidence level. A similar test showed the assumption of anisotropic temperature parameters to be significantly better than the isotropic model at the 0.5% confidence level.

Table I contains the final list of calculated and observed structure factors. The atomic positional and isotropic thermal parameters, along with their standard deviations as derived from the inverse matrix of the final least-squares refinement cycle, are given in Table II. The root-mean-square amplitudes of vibration derived from the thermal parameters are presented in Table III. The magnitudes of these values are reasonable. Entries are not shown in Tables II and III for the 15 phenyl hydrogen atoms, as these had their well-known spatial relationship to the

TABLE III

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

Atom	Minimum	Intermediate	Maximum
Cu	0.176	0.185	0.189
P	0.183	0.195	0.212
B	0.163	0.299	0.355
CA1	0.184	0.200	0.236
CA2	0.180	0.250	0.264
CA3	0.203	0.251	0.334
CA4	0.208	0.267	0.348
CA5	0.208	0.285	0.338
CA6	0.183	0.245	0.289
CB1	0.178	0.192	0.210
CB2	0.200	0.221	0.275
CB3	0.185	0.252	0.287
CB4	0.210	0.259	0.275
CB5	0.222	0.261	0.301
CB6	0.216	0.231	0.276
CC1	0.178	0.209	0.219
CC2	0.206	0.233	0.275
CC3	0.211	0.240	0.290
CC4	0.206	0.264	0.286
CC5	0.205	0.259	0.306
CC6	0.201	0.215	0.277

[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.

---

(19) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

carbon skeleton of the benzene rings. A perspective drawing of the molecule showing the atom-labeling scheme appears in Figure 1.

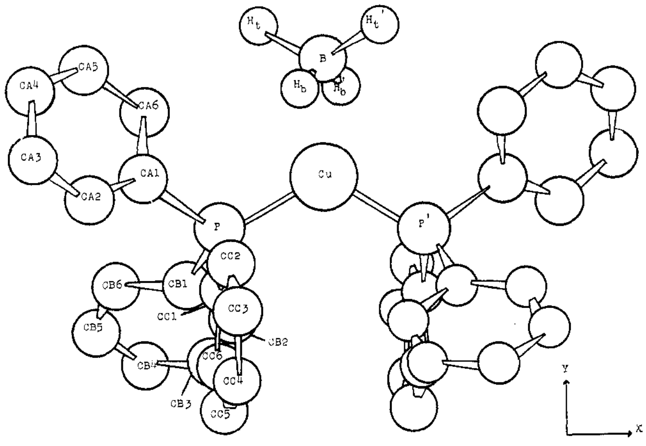


Figure 1.—Projection of borohydridobis(triphenylphosphine)-copper(I) showing the molecular structure. Phenyl hydrogen atoms are not shown.

Discussion

The crystal structure defined by the unit cell dimensions, symmetry operations, and parameters of Table II consists of loosely packed monomolecular units. The pertinent intramolecular distances and angles and their standard deviations are summarized in Table IV for all bonds to the copper and boron atoms. Table V contains similar information for the triphenylphosphine ligand, as well as the best least-squares planes through the carbon atoms of the benzene rings.

TABLE IV

INTERATOMIC DISTANCES (A) AND ANGLES (DEGREES) FOR ALL BONDS TO THE COPPER AND BORON ATOMS[a,b]

Interatomic distance		Angle	
Cu–P	2.276 (1)	P–Cu–P′	123.26 (6)
Cu–B	2.184 (9)	P–Cu–B	118.4 (1)
Cu–H_b	2.02 (5)	H_b–Cu–H_b′	69 (3)
B–H_b	1.26 (4)	P–Cu–H_b	100 (4)
B–H_t	1.37 (5)	P–Cu–H_b′	128 (4)
		H_b–B–H_b′	132 (5)
		H_t–B–H_t′	121 (5)
		H_b–B–H_t	95 (3)
		H_b–B–H_t′	109 (3)

[a] See Figure 1 for atom-labeling scheme. [b] Numbers in parentheses are estimated standard deviations.

The most important feature of the structure is the two-point attachment of the borohydride group to the copper atom (Figure 1), a result which is in agreement with both solution[13] and solid state[5,6] infrared spectral studies of the molecule. The coordination geometry of the copper atom may be described as quasi-tetrahedral, although a detailed examination of Table IV reveals significant departures from this idealized configuration. In particular, the angles about the copper atom deviate markedly from the tetrahedral value of 109.47°. These deviations result primarily from two effects (see Figure 1): (1) an opening up of the P–Cu–P′ angle which is due at least in part to steric interactions between the two phenyl rings B and C; (2) a rotation of the BH_4^- group about the crystallographic twofold axis passing through the copper and boron atoms. The second effect may originate in a steric interaction between the bridging hydrogen atoms and the protons on CA6 and CA6′. Calculations show the observed H–H distances to average 3.0 A, whereas a shorter H–H distance of 2.6 A would occur if the dihedral angle between the planes defined by P–Cu–P′ and H_b–B–H_b′ were 90°. The observed value for this angle is 115°. Rotation of the BH_4^- group in the direction opposite that shown in Figure 1 would only increase the H–H repulsive interaction. No indication of disorder in the BH_4^- group appeared on the Fourier maps.

TABLE V

DIMENSIONS OF THE TRIPHENYLPHOSPHINE GROUP[a,b]

Bond	Length, A	Angle	Deg	Angle	Deg
P–CA1	1.814 (5)	Cu–P–CA1	115.0 (2)	CA1–P–CB1	103.8 (2)
P–CB1	1.829 (4)	Cu–P–CB1	117.6 (1)	CA1–P–CC1	103.9 (2)
P–CC1	1.817 (4)	Cu–P–CC1	111.1 (2)	CB1–P–CC1	104.0 (2)

Best Plane Equation through Ring A

$$(0.0280)^{-1}X - (0.3751)^{-1}Y + (0.9266)^{-1}Z = 3.753$$

Distances (in A) of carbon atoms from plane					
CA1	−0.003	CA3	−0.002	CA5	−0.008
CA2	0.002	CA4	0.004	CA6	0.006

Bond	Length, A	Angle	Deg
CA1–CA2	1.398 (6)	P–CA1–CA2	122.9 (4)
CA2–CA3	1.389 (7)	CA1–CA2–CA3	120.2 (5)
CA3–CA4	1.381 (9)	CA2–CA3–CA4	120.1 (5)
CA4–CA5	1.375 (9)	CA3–CA4–CA5	119.7 (5)
CA5–CA6	1.373 (8)	CA4–CA5–CA6	120.1 (6)
CA6–CA1	1.378 (7)	CA5–CA6–CA1	121.6 (5)
		CA6–CA1–P	118.7 (3)

Best Plane Equation through Ring B

$$-(0.3787)^{-1}X + (0.7860)^{-1}Y + (0.4887)^{-1}Z = 1.906$$

Distances (in A) of carbon atoms from plane					
CB1	0.003	CB3	−0.006	CB5	0.009
CB2	0.003	CB4	0.000	CB6	−0.009

Bond	Length, A	Angle	Deg
CB1–CB2	1.368 (7)	P–CB1–CB2	119.3 (4)
CB2–CB3	1.389 (8)	CB1–CB2–CB3	122.5 (5)
CB3–CB4	1.337 (8)	CB2–CB3–CB4	119.1 (5)
CB4–CB5	1.392 (9)	CB3–CB4–CB5	121.6 (5)
CB5–CB6	1.415 (8)	CB4–CB5–CB6	118.1 (5)
CB6–CB1	1.378 (6)	CB5–CB6–CB1	120.6 (5)
		CB6–CB1–P	122.6 (4)

Best Plane Equation through Ring C

$$(0.9568)^{-1}X + (0.0165)^{-1}Y + (0.2903)^{-1}Z = 1.526$$

Distances (in A) of carbon atoms from plane					
CC1	0.008	CC3	0.004	CC5	0.002
CC2	−0.009	CC4	0.001	CC6	−0.006

Bond	Length, A	Angle	Deg
CC1–CC2	1.420 (7)	P–CC1–CC2	116.4 (3)
CC2–CC3	1.420 (8)	CC1–CC2–CC3	118.6 (4)
CC3–CC4	1.369 (8)	CC2–CC3–CC4	120.2 (5)
CC4–CC5	1.379 (8)	CC3–CC4–CC5	120.9 (5)
CC5–CC6	1.393 (8)	CC4–CC5–CC6	119.6 (5)
CC6–CC1	1.373 (6)	CC5–CC6–CC1	121.4 (5)
		CC6–CC1–P	124.0 (4)

[a] See Figure 1 for atom-labeling scheme; numbers given in parentheses refer to the standard deviation in the last significant figure listed. [b] Weighted least-squares planes were calculated with reference to an orthogonal coordinate system in which the Y axis is taken to be coincident with the cell b axis, the Z axis is in the direction $\vec{a} \times \vec{b}$, and the X axis is chosen according to the right-hand rule.

The boron atom may also be described as roughly tetrahedral, but again deviations occur (Table IV). Because of the large uncertainties in the hydrogen atom coordinates, however, it is difficult to attach much significance to the variations. The calculated dihedral angle between the planes defined by H_b–B–H_b' and H_t–B–H_t' is 98°. The average B–H distance is 1.31 ± 0.05 A which may be compared to values of 1.2 ± 0.2 A found for $Zr(BH_4)_4$[14] and 1.31 A (average) found for $(CH_3)_3NAl(BH_4)_3$.[20]

While it is difficult to assess the quantitative effects of intramolecular steric interactions on the observed geometry, qualitative arguments are sometimes sufficient. In the present case, the best defined deviation of the structure from the idealized tetrahedral configurations discussed above is the P–Cu–P′ angle of 123.26°. In certain other compounds containing *cis*-triphenylphosphine groups with metal–phosphorus distances comparable to that found here, considerably smaller P–M–P angles have been observed. For example, in $[(C_6H_5)_3P]_2Pt(CO_3)$, where the Pt–P bond lengths are 2.24 A, the P–Pt–P angle is 98.2°.[21] It is therefore tempting to suggest that, in $[(C_6H_5)_3P]_2Cu(BH_4)$, intramolecular steric interactions between the triphenylphosphine groups are not the sole cause of the large P–Cu–P′ angle. In particular, one might consider a delocalized bonding scheme in which direct Cu–B overlap might be significant. Such a description would require a greater fractional contribution of the copper 4s orbital to the bonding σ molecular orbitals than would a more conventional description in which two sp^3 orbitals from the copper atom would participate in two three-center, two-electron bonds with the borohydride group. Consistent with this proposal are the nearly trigonal P–Cu–P′ and P–Cu–B angles (Table IV) and the Cu–B distance of 2.184 A, which is not a great deal larger than the Cu–H distance of 2.02 A.[22] Cu–B distances of 2.1–2.3 A were also found in the crystal structure of $Cu_2B_{10}H_{10}$, in which "essentially covalent" Cu–B bonding interactions were suggested.[23] Further experimental work is currently in progress in an attempt to obtain a more definitive assessment of the bonding between the metal and the borohydride group.

Although a brief search of the literature did not reveal any other structurally characterized copper phosphine complexes, the value of 2.276 A for the Cu–P distance in the present compound seems reasonable. From the Cu(I)–Cl distance (2.16 A) found in $(CuCl)_3$[24] and from the difference (0.11 A) between the single-bond radii for chlorine and phosphorus,[25] we compute a Cu(I)–P distance of 2.27 A, in good agreement with the observed value. Table V contains detailed information about the geometry of the triphenylphosphine ligand. The average P–C bond length is 1.820 A. The individual carbon–carbon bond distances range from 1.337 to 1.420 A, with a mean value of 1.385 A. Although there appears to be no systematic variation in these distances, bond CB3–CB4 is unusually short. Excluding this distance from the averaging leads to a mean C–C bond length of 1.388 A, with a computed standard deviation from the mean of 0.017 A. The value of 1.337 A for the CB3–CB4 distance, therefore, lies just within the range of statistical significance (3σ). Best plane calculations through the phenyl rings show them to be planar as expected, the maximum deviation of any one carbon atom from the best plane being 0.009 A. The average values for the various angles within the ligand agree well with values found in other triphenylphosphine complexes.[26] Not reported in the table are the average (of 15 values) C–H distance, 1.04 ± 0.04 A, and H–C–C angle, 121 ± 2°.

Acknowledgments.—We wish to thank the National Science Foundation for support of this work under Grant GP-6758 and for an equipment grant (GP-6685) used to purchase our automated diffractometer.

---

[20] N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Chem. Commun.*, 286 (1966).

[21] F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *ibid.*, 408 (1967).

[22] A referee has pointed out that in diatomic Cu–H, the Cu–H distance is 1.46 A (G. Herzberg, "Molecular Spectra and Molecular Structure," 2nd ed, D. Van Nostrand Co., Inc., New York, N. Y., p 526), to which our Cu–H distance of 2.02 A may be compared. The longer distance found in our complex is consistent with the multicenter bonding suggested for the Cu–BH_4 linkage.

[23] A. Kaczmarczyk, R. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962).

[24] C.-H. Wong and V. Schomaker, *J. Phys. Chem.*, **61**, 358 (1957).

[25] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 225.

[26] *Cf.* S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965), and references contained therein.