from a neighboring Co atom whereas in an axial orientation it would have two. Relative to the Co–(CO) equatorial bonds, the Co–P bond is significantly bent closer to the Co_3 plane as illustrated, *e.g.*, by the reduction of the angle C(1)–Co(1)–P to 96° and the accompanying increase of the angle Co(3)–Co(1)–P to 162°. As a result a nice balance has been achieved in the nonbonded contacts between the phosphine group and external atoms, the four closest contacts involving four sterically distinct carbon atoms and all being in the range 3.17–3.39 Å. Thus C(4)···C(21) involves the equatorial carbon bonded to the same Co atom, C(5)···C(16) an equatorial carbon bonded to an adjacent Co atom, C(1)···C(16) the axial carbon bonded to the same Co atom, and C(10)···C(32) the terminal methyl group.

The terminal methyl group has been bent significantly away from the phosphine group as can be seen from the angles of the type C(10)–C(9)–Co. Otherwise the molecule (apart from the phosphine group) conforms to its idealized symmetry of C_{3v} as also observed in $CH_3CCo_3(CO)_9$[3] and $Co_3(CO)_{10}BH_2N(C_2H_5)_3$.[5] Likewise the molecular dimensions are in general agreement with those reported for these two compounds and for $[CCo_3(CO)_9]_2CO$.[6] However two particular features are to be noted. The Co–Co bonds in both the phosphine and borane derivatives are 0.03 Å longer than in the other two compounds. Also the Co–C(axial) bonds are systematically longer than the Co–C(equatorial) bonds in the phosphine and borane derivatives but not in the other two compounds. A better assessment of these differences can be made when similar bonds are compared in the related compounds whose detailed structures we have determined.

This structure determination supports the infrared spectral evidence[7] that there exists in solution a different isomer from that found in the solid state. On the other hand, these same spectral studies suggest a different solid-state structure (containing bridging carbonyls) for the $P(C_6H_{11})_3$ derivative, a structure analysis of which is in progress.

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E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE 1989

The Crystal Structure of the Tetramethylammonium Salt of the Octahydrotriborotetracarbonylchromium Anion, $(CO)_4CrB_3H_8^-$

BY L. J. GUGGENBERGER

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The crystal structure of tetramethylammonium octahydrotriborotetracarbonylchromium, $[(CH_3)_4N][(CO)_4CrB_3H_8]$, has been determined from three-dimensional X-ray counter data. The crystal structure consists of the packing of discrete $(CH_3)_4N^+$ cations and $(CO)_4CrB_3H_8^-$ anions. The $(CO)_4CrB_3H_8^-$ ion has an octahedrally hybridized chromium atom coordinated to two axial carbonyl groups, two equatorial carbonyl groups, and a B_3H_8 moiety bonded through two boron–hydrogen–chromium bonds with Cr–H distances of 1.78 Å. The equatorial and average axial Cr–C distances are 1.824 (7) and 1.900 (10) Å, respectively. Molecular orbital calculations indicate that the difference in equatorial and axial Cr–CO distances results from increased π bonding between the chromium atom and the equatorial carbonyl groups. Crystals of $[(CH_3)_4N][(CO)_4CrB_3H_8]$ are monoclinic, space group $P2_1/m$, with two formula units per cell of dimensions $a = 11.074 \pm 0.004$ Å, $b = 8.938 \pm 0.002$ Å, $c = 7.784 \pm 0.003$ Å, and $\beta = 98.12 \pm 0.04°$. The individual ions have space-group-imposed C_s point symmetry. The structure was refined by least squares to a conventional R of 0.077.

Introduction

The metal atom in metalloborane chemistry has a variety of different and sometimes novel roles. It can occupy a coordination site on the surface of a polyhedral boron fragment[1,2] linking two boron polyhedra in some cases, it may be the nucleus of a cation in forming complexes with borane anions,[3] or it may be coordinated to basic boron hydride fragments *via* metal–boron[4] or metal–hydrogen–boron bonds. The crystal and molecular structures of $[(CH_3)_4N][(CO)_4CrB_3H_8]$ reported here exemplify the latter case wherein a $B_3H_8^-$ moiety is bonded to a chromium atom *via* Cr–H–B bonds. A preliminary account of this work was reported earlier.[5]

Another case of metal–hydrogen–boron bonding occurs with the borohydride ion, BH_4^-, which bonds to metal atoms through double hydrogen bridges in cases such as $(H_3C)_3N \cdot Al(BH_4)_3$[6] and $[(C_6H_5)_3P]_2CuBH_4$[7] and apparently through triple hydrogen bridges in

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(1) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1968.

(2) M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

(3) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2272 (1968).

(4) G. W. Parshall, *J. Am. Chem. Soc.*, **86**, 361 (1964).

(5) F. Klanberg and L. J. Guggenberger, *Chem. Commun.*, 1293 (1967).

(6) N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *ibid.*, 286 (1966).

(7) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967).

$Zr(BH_4)_4$.[8] Reference 9 gives a more extensive list of references to work involving BH_4^- bonded to transition metals. A novel case of metal–hydrogen–boron bonding occurs in $Mn_3(CO)_{10}(BH_3)_2$ where each boron is linked to three different Mn atoms through Mn–H–B bonds.[10] The preparation, properties, and spectral data for the $B_3H_8^-$ metal adducts have been reported earlier.[3] In addition to the isostructural Cr, Mo, and W carbonyls of $(CO)_4MB_3H_8^-$, the compounds $[(C_6H_5)_3P]_2MB_3H_8$ [M = Cu, Ag] and $(C_5H_5)_2TiB_3H_8$ also exist as stable entities. The chemistry of the $Cu–B_3H_8$ system has been studied independently by Lippard and Ucko.[9] Lippard and Melmed have determined the crystal structure of $[(C_6H_5)_3P]_2Cu(B_3H_8)$.[11]

Crystal Data and Structure Determination

Crystals of tetramethylammonium octahydrotriborotetracarbonylchromium, $[(CH_3)_4N][(CO)_4CrB_3H_8]$, are isomorphous with the molybdenum and tungsten compounds with unit cell data as summarized in Table I. The cell parameters were obtained from a least-squares refinement of powder data recorded on a Hägg–Guinier camera using a KCl internal standard ($a_{25°}$ = 6.2931 Å). The observed densities were obtained by the displacement method; the calculated densities are based on two formula units per cell. The only systematic absence observed on Weissenberg and precession films was $0k0$, $k = 2n + 1$. The possible space groups are $P2_1/m$ or $P2_1$. The correct space group based on this refinement is $P2_1/m$ (*vide infra*). Both anions and cations are required to have $C_s(m)$ point symmetry. Atoms were placed in the general positions $\pm(x, y, z; x, \frac{1}{2} - y, z)$ or the special positions $\pm(x, \frac{1}{4}, z)$.[12]

The $[(CH_3)_4N][(CO)_4CrB_3H_8]$ compound was chosen for this structure investigation to minimize the metal atom contributions to the intensities. The crystal chosen for data collection was a thin platelet of dimensions 0.08 × 0.22 × 0.53 mm; the effective length was considerably shorter than 0.53 mm since the crystal

TABLE I

CELL DATA FOR $[(CH_3)_4N][(CO)_4MB_3H_8]$ COMPOUNDS

	Cr	Mo	W
a, Å	11.074 (4)	11.249 (2)	11.214 (2)
b, Å	8.938 (2)	8.896 (2)	8.896 (2)
c, Å	7.784 (3)	7.812 (2)	7.799 (2)
β, deg	98.12 (4)	98.20 (2)	98.33 (2)
ρ_{obsd}, g/cm³	1.22	1.37	1.84
ρ_{calcd}, g/cm³	1.22	1.38	1.77
Space group	$P2_1/m$	$P2_1/m^a$	$P2_1/m^a$

[a] Although the space group was confirmed only for the Cr compound, the close similarity in the diffraction photographs of the Cr, Mo, and W compounds strongly suggests that the space group for the Mo and W compounds is also $P2_1/m$ (instead of $P2_1$).

TABLE II

POSITIONAL AND THERMAL PARAMETERS FOR $[(CH_3)_4N][(CO)_4CrB_3H_8]^a$

Atom	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.2297 (1)	0.25	0.0076 (2)	0.0076 (1)	0.0135 (2)	0.0175 (3)	0.0	0.0020 (1)	0.0
C_1	0.3128 (8)	0.25	−0.1893 (14)	0.0093 (9)	0.0175 (16)	0.0278 (25)	0.0	0.0040 (13)	0.0
O_1	0.3703 (6)	0.25	−0.2992 (11)	0.0145 (8)	0.0288 (16)	0.0335 (19)	0.0	0.0116 (11)	0.0
C_2	0.1595 (9)	0.25	0.2171 (14)	0.0122 (10)	0.0256 (21)	0.0172 (21)	0.0	0.0001 (12)	0.0
O_2	0.1304 (7)	0.25	0.3493 (11)	0.0190 (10)	0.0513 (25)	0.0180 (16)	0.0	0.0044 (11)	0.0
C_3	0.3319 (6)	0.3967 (8)	0.1043 (9)	0.0105 (6)	0.0159 (11)	0.0255 (16)	−0.0003 (7)	0.0009 (8)	−0.0017 (11)
O_3	0.3980 (5)	0.4867 (6)	0.1696 (8)	0.0147 (6)	0.0221 (10)	0.0413 (15)	−0.0029 (6)	−0.0017 (8)	−0.0088 (10)
B_1	−0.0729 (9)	0.25	−0.0900 (16)	0.0084 (10)	0.0225 (23)	0.0206 (24)	0.0	0.0052 (13)	0.0
B_2	0.0504 (6)	0.3495 (9)	−0.1728 (10)	0.0092 (7)	0.0158 (12)	0.0195 (15)	0.0012 (8)	0.0028 (8)	−0.0004 (12)
N	0.7041 (6)	0.25	0.3740 (9)	0.0088 (7)	0.0189 (13)	0.0209 (16)	0.0	0.0034 (9)	0.0
C_4	0.6589 (11)	0.25	0.1801 (14)	0.0148 (13)	0.0686 (49)	0.0146 (21)	0.0	0.0021 (13)	0.0
C_5	0.6041 (12)	0.25	0.4745 (18)	0.0161 (16)	0.1006 (78)	0.0263 (31)	0.0	0.0083 (19)	0.0
C_6	0.7814 (17)	0.3766 (18)	0.4243 (18)	0.0619 (34)	0.0564 (38)	0.0443 (32)	−0.0438 (31)	−0.0096 (28)	0.0113 (30)
H_1	0.1315 (53)	0.4039 (71)	−0.0541 (85)	4.0					
H_2	0.0464 (53)	0.4008 (75)	−0.2979 (94)	4.0					
H_3	−0.0243 (57)	0.3972 (76)	−0.1007 (85)	4.0					
H_4	−0.1610 (84)	0.25	−0.2046 (125)	4.0					
H_5	−0.0966 (76)	0.25	0.0499 (129)	4.0					

[a] The standard deviations of the least significant digits are given in parentheses except for the arbitrarily fixed temperature factors of the hydrogen atoms and those fixed by symmetry. The anisotropic thermal ellipsoid is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

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

(9) S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, **7**, 1051 (1968).

(10) H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2753 (1965).

(11) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8**, 2755 (1969).

(12) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, p 93.

extended to sharp points in this, the b^*, direction. The crystal was mounted on a Picker four-circle automatic diffractometer equipped with a scintillation detector and a pulse-height discriminator with the b^* axis conincident with the ϕ axis of the diffractometer. The data were measured using Zr-filtered Mo radiation (λ 0.7107Å) and the θ–2θ scan technique. Individual backgrounds of 20 sec were recorded before and after each scan which covered 2° (1°/min) plus the angular separation of $K\alpha_1$ and $K\alpha_2$. A total of 1215 reflections, including both $hk0$ and $\bar{h}k0$ data, were measured out to a 2θ of 45°.

The corrections for the Lorentz and polarization effects were applied in the usual way. An absorption correction was applied using the program ACACA.[13] The crystal was defined by eight plane faces for the absorption correction. The linear absorption coefficient for Mo $K\alpha$ radiation is 7.9 cm^{-1}. The minimum and maximum calculated transmission factors were 0.85 and 0.94, respectively. The structure factor errors were assigned according to a scheme reported earlier.[14] Those structure factors which were less than their estimated standard deviations were called "unobserved."

The structure solution was initiated assuming the noncentric space group $P2_1$. The Cr atom position was determined from a Patterson function. The R value ($\Sigma||F_o| - |F_c||/\Sigma|F_o|$) was 0.477 based on the Cr atom position only. The remaining nonhydrogen atom positions were determined from a combination of Patterson superposition and heavy-atom techniques. The R was reduced to 0.120 after four least-squares cycles varying the positional and isotropic thermal parameters with all the nonhydrogen atoms included in the structure factor calculations. It was clear from the isotropic temperature factors that there was large thermal motion associated with the methyl carbon atoms of the tetramethylammonium group. The R was 0.091 after three cycles of least squares with anisotropic thermal parameters.

A study of the atom positions indicated that the molecule possessed a mirror plane within the errors involved. Hence all further refinements were carried out in the centric space group $P2_1/m$. The $hk0$ and $\bar{h}k0$ data were averaged at this point, and an electron density difference map was calculated from which all the hydrogen atoms were easily located. The hydrogen atom positional parameters were included in the final refinement but not the temperature factors which were set equal to 4.0 Å^2. The refinement was stopped after three more cycles of least squares. The convergence and the reasonable final locations of the hydrogen atoms appear to justify their inclusion in the refinement. In an intermediate refinement the hydrogen atom temperature factors were varied with reasonable results (B's varied from 0.5 to 4.6 Å^2). The final R values for the 990 observed reflections were 0.077 for R and 0.086 for wR, where wR is $\{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$. The maximum and minimum peaks in the final electron density difference map were 0.6 and −0.3 $e^-/Å^3$, respectively, both in the vicinity of the methyl carbon atoms which have very large anisotropic thermal parameters. No attempt was made to locate the methyl hydrogen atoms in view of the large thermal parameters of the methyl carbon atoms.

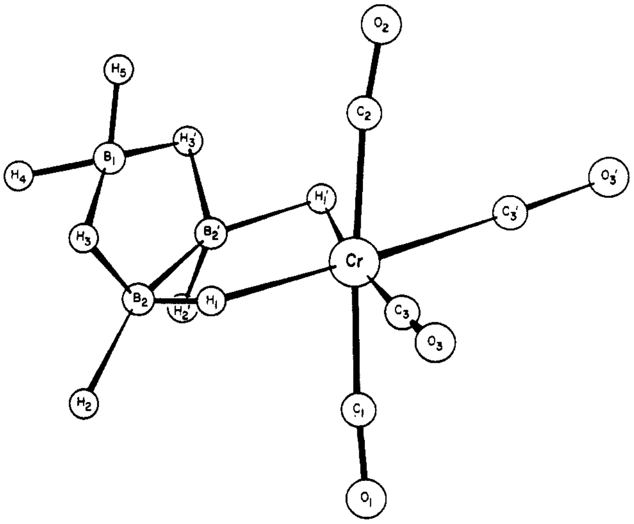

Figure 1.—The molecular configuration of $(CO)_4CrB_3H_8^-$.

The atomic scattering factors used were those for the neutral atoms.[15] The real and imaginary parts of the anomalous scattering effect for the Cr atom were included in the calculated structure factors using values reported by Templeton.[16] The function minimized in least squares was $\Sigma w(|F_o| - |F_c|)^2$.

The final refined parameters are given in Table II. The shifts in the final least-squares cycle were less than 0.1 of the associated standard deviations. The observed and calculated structure factors are given in Table III where an asterisk is used to denote an unobserved reflection.

Structure Description and Discussion

The crystal structure of $[(CH_3)_4N][(CO)_4CrB_3H_8]$ consists of the packing of tetramethylammonium cations and octahydrotriborotetracarbonylchromium anions. The molecular configuration of the $(CO)_4CrB_3H_8^-$ anion is shown in Figure 1. The anion possesses $C_s(m)$ point symmetry; the atoms on the molecular and crystallographic mirror plane are Cr, C_1, O_1, C_2, O_2, B_1, H_4, and H_5. The numbering system is such that the primed atoms are related to the unprimed atoms by the mirror plane.

A set of interatomic distances and angles is given in Table IV. Distances and angles not listed are related to those listed by the molecular mirror plane. The covariances were included in the estimates of the errors.

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(13) C. T. Prewitt, local unpublished computer program, 1968. Other programs used in this work include Prewitt's least-squares program SFLS5, the Busing–Levy error function program ORFFE, the Fourier program FOUR written originally by C. J. Fritchie, Jr., a local superposition function program, and the Johnson crystallographic plotting program ORTEP.

(14) L. J. Guggenberger, *Inorg. Chem.*, **7**, 2260 (1968).

(15) H. P. Hansen, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, **17**, 1040 (1964).

(16) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10) FOR $[(CH_3)_4N][(CO)_4CrB_3H_8]$

K,L= 0, 0		
2	702	614
3	341	324
4	175	154
5	205	198
6	115	133
7	168	176
9	63	63
10	34	35
11	133	134
K,L= 1, 0		
1	495	571
2	213	174
3	166	160
4	104	113
5	88	83
6	186	188
7	79	73
8	135	128
9	107	108
10	134	132
11	32	28
K,L= 2, 0		
0	919	902
1	286	282
2	534	534
3	109	108
4	165	175
5	26	27*
6	38	48
7	144	145
8	51	39
9	91	99
10	51	46
11	78	75
K,L= 3, 0		
1	347	316
2	218	227
3	372	364
4	272	290
5	137	137
8	99	103
9	80	91
10	82	82
11	28	3
K,L= 4, 0		
0	523	552
1	137	138
2	284	295
3	67	59
4	7	13*
5	137	136
6	154	155
7	51	53
8	93	90
9	45	48
10	21	22
K,L= 5, 0		
1	264	278
2	0	10*
3	172	178
4	212	222
5	42	35
6	94	94
7	95	104
8	89	87
9	23	39
10	85	76
K,L= 6, 0		
0	276	275
1	2	19*
2	266	264
3	18	13*
4	113	119
5	38	16
6	32	29
7	60	64
8	45	28
9	79	86
K,L= 7, 0		
1	148	158
2	27	11
3	112	122
4	45	38
5	31	9
7	26	20
8	79	75
K,L= 8, 0		
0	189	196
1	0	3*
2	110	108
3	17	5*
4	37	47
5	50	39
6	56	44
K,L= 9, 0		
1	82	76
2	25	14*
3	37	40
4	39	33
K,L= 0, 1		
-11	133	129
-10	61	49
-9	130	137
-8	49	43
-7	333	333
-6	196	188
-5	44	51
-4	91	88
-3	283	253
-1	0	50*
0	544	594
2	297	303
3	79	92
4	473	466
5	232	237
6	142	114
7	107	119
8	30	15
9	123	128
10	72	62
11	87	81
K,L= 1, 1		
-11	25	2
-10	116	114
-9	12	10*
-8	124	123
-7	165	169
-6	86	91
-5	274	292
-4	93	79
-3	269	264
-2	214	193
0	208	151
1	644	612
2	370	335
3	626	615
4	214	192
5	164	186
6	213	213
7	36	9
8	83	76
9	71	64
10	113	116
11	0	2*
K,L= 2, 1		
-11	91	105
-10	45	59
-9	152	159
-8	17	17
-7	193	195
-6	245	246
-5	118	128
-4	289	280
-3	279	285
-2	263	269
-1	22	23
0	178	172
1	486	487
2	900	891
3	11	31*
4	504	487
5	55	44
6	72	67
7	191	195
8	68	68
9	86	87
10	56	48
11	48	38
K,L= 3, 1		
-11	43	19
-10	92	95
-9	51	53
-8	71	75
-7	166	162
-6	101	102
-5	258	259
-4	231	226
-3	159	181
-2	34	34
-1	76	41
0	37	27
1	381	397
2	83	72
3	461	471
4	119	122
5	175	181
6	110	109
7	59	54
8	64	54
9	36	14
10	70	59
K,L= 4, 1		
-10	43	26
-9	88	93
-8	109	118
-7	175	178
-6	107	119
-5	257	273
-4	72	70
-3	31	36
-2	50	45
-1	33	38
0	259	255
1	28	14
2	406	419
3	290	301
4	319	322
5	112	109
6	236	241
7	69	70
8	0	22*
9	65	60
10	0	5*
K,L= 5, 1		
-10	91	86
-9	53	47
-8	42	56
-7	103	109
-6	68	72
-5	113	117
-4	125	107
-3	209	218
-2	45	53
-1	159	160
0	85	84
1	265	265
2	9	8*
3	246	250
4	89	77
5	131	125
6	29	20
7	51	52
8	62	71
9	0	4*
K,L= 6, 1		
-9	96	100
-8	22	17
-7	70	58
-6	19	35
-5	81	75
-4	113	117
-3	64	72
-2	39	42
-1	33	17
0	148	156
1	77	72
2	279	293
3	71	64
4	102	105
5	28	32
6	54	52
7	126	120
8	48	35
K,L= 7, 1		
-8	62	62
-7	46	33
-6	29	24
-5	77	79
-4	60	54
-3	151	146
-2	29	27
-1	145	138
0	0	5*
1	190	186
2	27	34
3	145	151
4	23	8
5	35	39
6	52	60
7	45	33
K,L= 8, 1		
-6	40	40
-5	34	35
-4	46	31
-3	24	6
-2	70	72
-1	24	13
0	117	119
1	27	7
2	78	82
3	31	35
4	69	74
5	39	49
6	41	55
K,L= 9, 1		
-4	36	31
-3	18	42
-2	11	25*
-1	67	84
0	40	5
1	62	60
2	25	8
3	69	77
K,L= 0, 2		
-11	69	70
-10	53	32
-9	116	118
-8	88	86
-7	193	204
-6	133	140
-5	96	107
-4	377	380
-3	257	241
-2	835	804
-1	510	485
0	108	109
1	329	303
2	29	27
4	432	423
5	121	118
7	106	94
8	66	69
9	176	169
10	41	8
11	49	55
K,L= 1, 2		
-11	47	34
-10	146	148
-9	0	6*
-8	243	247
-7	37	29
-6	39	35
-5	103	107
-4	89	89
-3	598	561
-2	118	113
-1	406	391
0	249	229
1	180	155
2	16	20
3	333	357
4	167	171
5	276	286
6	131	145
7	161	157
8	112	112
9	101	95
10	85	77
K,L= 2, 2		
-11	83	80
-10	33	41
-9	92	92
-8	70	65
-7	128	134
-6	295	278
-5	277	281
-4	277	289
-3	316	301
-2	55	75
-1	105	76
0	220	216
2	316	301
3	33	30
4	226	219
6	204	216
7	141	139
8	98	94
9	72	85
10	35	23
K,L= 3, 2		
-11	27	23
-9	50	54
-8	178	178
-7	45	52
-6	174	185
-5	128	135
-4	189	208
-3	247	223
-2	60	55
-1	176	161
0	130	140
1	213	231
2	94	104
4	56	60
5	354	353
6	96	99
7	133	140
10	60	53
K,L= 4, 2		
-10	69	71
-9	70	71
-8	106	93
-7	178	177
-6	114	103
-5	167	162
-4	240	256
-3	33	5
-2	162	183
-1	173	168
0	72	78
1	87	89
2	102	98
3	194	191
4	276	268
5	31	10
6	189	192
7	67	60
8	21	16
9	80	79
K,L= 5, 2		
-10	100	99
-9	45	50
-8	102	106
-7	19	11
-6	125	127
-5	66	70
-4	74	72
-3	177	179
-2	51	65
-1	127	123
0	33	28
1	138	145
2	147	141
3	208	213
4	54	58
5	227	230
6	76	78
7	70	78
8	63	71
9	43	30
K,L= 6, 2		
-9	59	62
-8	42	28
-7	60	55
-6	102	98
-5	115	111
-4	207	212
-3	76	65
-2	97	101
-1	86	75
0	166	163
1	25	18
2	136	131
3	26	2
4	43	47
5	47	38
6	99	103
7	111	106
8	48	48
K,L= 7, 2		
-7	47	23
-6	48	34
-5	60	66
-4	49	47
-3	93	102
-2	34	23
-1	109	108
0	27	4
1	102	104
2	31	5
3	78	75
4	59	60
5	82	81
6	89	82
7	55	64
K,L= 8, 2		
-6	57	40
-5	53	42
-4	85	79
-3	41	39
-2	105	103
-1	62	58
0	58	64
1	44	21
2	58	52
3	49	39
4	75	76
5	56	38
K,L= 9, 2		
-3	51	50
-2	0	22*
-1	64	55
0	29	18
1	8	31*
2	36	21
K,L= 0, 3		
-11	54	63
-10	29	6
-9	151	157
-8	63	60
-7	92	84
-6	56	51
-5	35	23
-4	441	441
-3	208	208
-2	492	490
-1	229	226
0	8	34*
1	156	151
2	236	235
3	322	326
4	122	134
5	30	28
6	151	153
7	93	92
8	163	162
9	104	104
10	0	37*
K,L= 1, 3		
-11	28	11
-10	74	68
-9	67	70
-8	175	183
-7	216	209
-6	165	170
-5	64	71
-4	253	241
-3	255	257
-1	479	452
0	256	240
1	219	216
2	109	107
3	72	74
4	164	169
5	78	74
6	150	139
7	157	160
8	127	121
9	81	89
10	82	73
K,L= 2, 3		
-11	74	72
-10	32	6
-9	106	101
-8	70	80
-7	149	152
-6	126	129
-5	200	216
-4	137	132
-3	65	65
-2	279	277
-1	36	35
0	414	431
1	80	79
2	229	235
3	109	98
4	75	79
6	205	209
7	47	37
8	128	126
9	51	57
10	43	2
K,L= 3, 3		
-10	56	53
-9	86	79
-8	170	173
-7	175	164
-6	228	227
-5	70	70
-4	144	133
-3	69	78
-2	25	17
-1	328	340
0	19	6
1	239	244
2	3	11*
3	100	90
4	102	91
5	128	128
6	106	103
7	70	71
8	72	68
9	49	43
K,L= 4, 3		
10	52	51
-9	66	82
-8	0	22*
-7	171	176
-6	43	45
-5	74	93
-4	160	149
-3	52	59
-2	175	163
-1	126	133
0	207	219
1	103	108
2	218	230
3	47	46
4	213	225
5	26	24
6	103	108
7	64	53
8	35	50
9	63	64
K,L= 5, 3		
-9	51	49
-8	103	105
-6	155	145
-4	81	74
-3	123	131
-1	191	202
0	0	10*
1	118	128
2	35	38
3	69	63
4	25	5
5	90	86
6	109	103
7	24	39
8	50	58
K,L= 6, 3		
-8	24	13
-7	66	70
-6	62	71
-5	86	85
-4	102	103
-3	0	14*
-2	109	106
-1	45	48
0	194	200
1	0	18*
2	75	70
3	0	23*
4	58	56
5	84	86
6	110	109
7	57	63
K,L= 7, 3		
-7	67	53
-6	77	78
-5	98	85
-4	87	75
-3	97	95
-2	90	79
-1	127	134
0	65	57
1	52	51
2	16	11
3	0	14*
4	55	56
5	87	72
6	63	68
K,L= 8, 3		
-5	27	38
-4	80	81
-3	30	27
-2	98	88
-1	44	31
0	64	54
1	26	1
2	67	65
3	44	39
4	64	59
K,L= 0, 4		
-11	77	79
-10	15	22
-9	73	68
-8	61	65
-7	58	53
-6	149	149
-5	302	305
-4	349	357
-3	250	260
-2	116	107
-1	190	154
0	10	39*
1	125	125
2	227	255
3	85	84
4	46	53
5	99	97
6	110	113
7	144	133
8	118	120
9	71	54
K,L= 1, 4		
-11	44	43
-10	48	57
-9	29	15
-8	52	63
-7	83	100
-6	129	121
-5	251	249
-4	205	197
-3	258	257
-2	70	73
-1	176	181
0	24	23
1	346	330
2	41	37
3	228	233
5	96	98
6	51	62
7	63	66
8	63	70
9	51	35
K,L= 2, 4		
-10	22	4
-9	62	61
-8	80	82
-7	141	142
-6	101	100
-5	276	269
-4	146	151
-3	23	21
-2	205	213
-1	54	59
0	200	217
1	177	169
2	131	138
3	112	117
4	95	97
5	123	122
6	120	118
7	69	59
8	73	61
9	81	69
K,L= 3, 4		
-10	42	42
-9	0	17*
-8	102	110
-7	70	77
-6	125	129
-5	119	114
-4	95	93
-3	145	135
-2	35	44
-1	256	257
0	33	11
1	288	284
2	48	57
3	211	223
4	29	49
5	99	98
6	0	24*
8	48	52
K,L= 4, 4		
-9	75	67
-8	40	15
-7	112	120
-6	112	105
-5	138	132
-4	140	146
-3	124	123
-2	108	122
-1	0	3*
0	161	167
1	42	48
2	192	197
3	64	20
5	65	61
6	16	6
7	61	75
8	63	58
K,L= 5, 4		
-9	0	27*
-8	57	67
-7	54	58
-6	67	64
-5	113	116
-4	72	66
-3	90	73
-2	96	94
-1	195	185
0	50	40
1	155	165
2	47	50
3	120	136
4	40	16
5	65	70
6	62	66
7	33	30
K,L= 6, 4		
-8	22	22
-7	84	79
-6	92	84
-5	109	104
-4	85	80
-3	95	94
-2	121	122
-1	62	57
0	99	106
1	46	27
2	41	34
3	44	36
4	75	63
5	86	78
6	68	56
K,L= 7, 4		
-6	45	42
-5	80	80
-4	39	40
-3	83	84
-2	66	65
-1	113	116
0	17	22
1	58	57
2	32	10
3	63	62
4	32	34
5	76	67
K,L= 8, 4		
-4	68	66
-3	54	58
-2	46	47
-1	43	32
0	50	40
1	28	3
2	68	64
K,L= 0, 5		
-9	69	65
-7	0	25*
-6	47	51
-5	185	149
-4	290	280
-3	206	205
-2	206	209
-1	63	68
0	236	241
1	10	31*
2	217	218
3	24	8
4	74	72
5	22	32
6	71	88
7	72	74
8	29	42
K,L= 1, 5		
-10	80	82
-9	25	13
-8	50	56
-7	45	22
-6	132	141
-5	122	113
-4	159	167
-3	121	107
-2	152	155
-1	119	134
0	34	20
1	146	148
2	126	114
3	106	108
4	38	27
5	183	181
6	63	50
7	88	78
8	42	33
K,L= 2, 5		
-10	27	12
-9	84	86
-8	9	2*
-7	29	30
-6	18	15
-5	63	65
-4	196	203
-3	106	105
-2	301	298
-1	137	145
0	207	199
1	48	43
2	156	150
3	24	18
4	121	120
5	24	5
6	30	41
7	41	38
8	27	12
K,L= 3, 5		
-9	59	13
-8	140	107
-7	27	13
-6	76	73
-5	48	48
-4	82	76
-3	115	129
-2	94	95
-1	198	196
0	26	11
1	152	154
2	39	43
3	138	148
4	34	21
5	102	94
6	49	41
7	36	33
K,L= 4, 5		
-9	81	79
-8	0	4*
-7	35	20
-6	38	30
-5	24	42
-4	106	101
-3	110	114
-2	192	183
-1	41	17
0	179	173
1	53	65
2	157	166
3	63	67
4	65	62
5	13	30*
6	38	7
7	33	35
K,L= 5, 5		
-8	87	84
-7	54	39
-6	64	47
-5	43	44
-4	91	92
-3	78	77
-2	81	79
-1	137	141
0	41	13
1	97	97
2	23	7
3	100	97
4	58	50
5	65	58
6	56	38
K,L= 6, 5		
-6	44	40
-5	38	31
-4	72	71
-3	78	78
-2	141	138
-1	68	42
0	73	62
1	39	31
2	73	77
3	29	30
4	81	86
K,L= 7, 5		
-5	54	37
-4	60	53
-3	31	49
-2	63	70
-1	51	54
0	39	7
1	49	44
2	35	32
K,L= 0, 6		
-9	85	88
-7	139	138
-6	52	25
-5	80	89
-4	54	44
-3	0	6*
-2	64	51
-1	35	37
0	192	206
1	35	22
2	129	135
3	0	11*
4	138	134
5	65	53
6	85	89
7	38	11
K,L= 1, 6		
-9	31	23
-8	83	89
-7	42	40
-6	79	88
-5	114	126
-4	0	29*
-3	55	53
-2	155	171
-1	127	132
0	96	93
1	167	161
2	39	45
3	99	98
4	22	25
5	96	109
6	60	47
K,L= 2, 6		
-9	106	113
-8	56	32
-7	101	106
-6	32	15
-5	32	29
-4	34	18
-3	5	11*
-2	107	112
-1	66	60
0	144	151
1	0	17*
2	156	162
3	0	17*
4	125	130
6	48	45
K,L= 3, 6		
-8	83	90
-7	42	27
-6	36	38
-5	67	66
-4	27	22
-3	99	92
-2	98	105
-1	127	119
0	93	102
1	132	130
2	31	27
3	70	82
4	21	15
5	51	36
6	39	37
K,L= 4, 6		
-7	51	58
-6	23	10
-5	49	49
-4	26	17
-3	0	18*
-2	110	116
-1	0	3*
0	118	131
1	73	75
2	127	132
3	26	14
4	53	61
5	18	49
K,L= 5, 6		
-6	27	38
-5	35	31
-4	30	43
-3	78	74
-2	33	37
-1	80	80
0	66	67
1	77	83
2	32	18
3	62	66
4	41	32
K,L= 6, 6		
-4	37	23
-3	45	44
-2	71	61
-1	6	12*
0	37	35
1	36	11
2	89	92
K,L= 0, 7		
-7	120	130
-6	92	94
-5	116	116
-4	35	23
-3	88	81
-2	51	43
-1	21	22
0	48	52
1	16	4
2	71	87
3	0	33*
4	130	136
5	46	34
K,L= 1, 7		
-7	26	27
-6	119	120
-5	64	63
-4	16	15
-3	52	41
-2	10	4*
-1	82	86
0	0	14*
1	69	69
2	37	31
3	104	93
4	49	3
K,L= 2, 7		
-7	87	87
-6	82	70
-5	91	95
-4	62	63
-3	77	80
-2	30	38
-1	0	4*
0	35	35
1	0	15*
2	92	89
3	48	34
4	92	85
K,L= 3, 7		
-6	81	80
-5	49	61
-4	53	25
-3	70	73
-2	32	4
-1	61	70
0	48	48
1	92	89
2	0	27*
3	52	60
K,L= 4, 7		
-5	82	86
-4	72	69
-3	34	31
-2	65	52
-1	16	20
0	26	37
1	43	49
2	54	50
K,L= 5, 7		
-3	55	54
-2	23	3
-1	39	35
0	54	39
K,L= 0, 8		
-5	59	58
-4	41	23
-3	93	90
-2	104	106
-1	40	12
0	47	39
1	36	15
K,L= 1, 8		
-4	88	90
-3	49	59
-2	52	43
-1	54	62
0	22	10
1	54	49
K,L= 2, 8		
-4	60	46
-3	92	83
-2	77	83
-1	17	8
0	56	52

No thermal motion corrections were applied to the distances in Table IV. The thermal motion correction assuming the second atom rides on the first[17] would add only about 0.01 Å to the Cr–C distances but considerably more to the N–C distances in view of the large thermal parameters of the methyl carbon atoms. However, the average observed N–C distance of 1.46 Å compares well with 1.47 Å which is the sum of the covalent radii.[18]

Two types of Cr–C distances are observed, namely, equatorial distances (Cr–C_3) of 1.824 (7) Å and an average axial distance (Cr–C_1) of 1.900 (10) Å. The differences in Cr–C distances appear to result quite naturally from the nature of the bonding involved rather than from any unusual steric interactions (*vide infra*). Both these distances are in the range of documented Cr–C distances of this type. Other Cr–C distances observed are 1.81 (1) Å in tricarbonyl-*exo*-7-phenylcyclohepta-1,3,5-trienechromium[19] and hexamethylbenzenetricarbonylchromium,[20] 1.82 (1) Å in tricarbonyl-1,6-methanocyclodecapentaenechromium,[21] 1.88 (1) Å in phenylmethoxycarbenepentacarbonylchromium,[22] and 1.91 (1) Å in hexacarbonylchromium.[23] The bonding effects that give rise to different Cr–C distances also lead to two different C–O distances, *i.e.*, 1.16 (1) and 1.13 (1) Å for the equatorial and axial C–O distances, respectively.

There are few metal–hydrogen distances available for comparison with the 1.78 (6) Å distance observed for Cr–H. This distance is similar, however, to the Cr–H distance of 1.70 (1) Å observed in $HCr_2(CO)_{10}^-$ which has a linear Cr–H–Cr three-center, two-electron bonding configuration.[24] Handy, *et al.*, have pointed out that observed terminal M–H distances are consistent with distances estimated by taking half the metal–metal bond length plus a value of 0.2 Å for the hydrogen radius.[24] The empirically estimated Cr–H distance based on the preceding formula is 1.70 Å.

The geometry of the B_3H_8 portion of this structure can be compared with the structure of the isolated

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TABLE IV

SELECTED INTERATOMIC DISTANCES AND ANGLES FOR $[(CH_3)_4N][(CO)_4CrB_3H_8]$[a]

Distance	Value, Å	Angle	Value, deg
$Cr-C_1$	1.896 (11)	C_1-Cr-C_3	89.4 (3)
$Cr-C_2$	1.904 (12)	C_1-Cr-C_2	175.2 (4)
$Cr-C_3$	1.824 (7)	C_2-Cr-C_3	87.2 (3)
$Cr-O_1$	3.029 (8)	C_3-Cr-C_3'	91.9 (4)
$Cr-O_2$	3.018 (9)	C_1-Cr-H_1	97 (2)
$Cr-O_3$	2.980 (6)	C_2-Cr-H_1	86 (2)
$Cr-H_1$	1.78 (6)	C_3-Cr-H_1	83 (2)
C_1-O_1	1.14 (1)	H_1-Cr-H_1'	101 (4)
C_2-O_2	1.12 (1)	$Cr-C_1-O_1$	175.0 (9)
C_3-O_3	1.16 (1)	$Cr-C_2-O_2$	172.6 (9)
C_1-C_3	2.62 (1)	$Cr-C_3-O_3$	177.9 (6)
C_2-C_3	2.57 (1)	$Cr-H_1-B_2$	104 (4)
C_3-C_3'	2.62 (1)	$H_1-B_2-B_2'$	112 (3)
C_3-H_1	2.38 (6)	$H_1-B_2-H_2$	115 (4)
B_1-B_2	1.82 1)	$H_1-B_2-H_3$	89 4)
B_1-H_3	1.43 (7)	$H_2-B_2-B_2'$	115 (4)
B_1-H_4	1.22 (9)	$H_2-B_2-H_3$	110 (5)
B_1-H_5	1.16 (10)	$H_3-B_2-B_2'$	112 (3)
B_2-B_2'	1.78 (1)	$B_1-H_3-B_2$	89 (4)
B_2-H_1	1.29 (6)	$H_3-B_1-H_3'$	134 (5)
B_2-H_2	1.07 (7)	$H_3-B_1-H_4$	103 (3)
B_2-H_3	1.15 (7)	$H_3-B_1-H_5$	101 (3)
H_4-H_5	2.01 (13)	$H_4-B_1-H_5$	115 (6)
H_3-H_3'	2.63 (14)	C_4-N-C_5	111.5 (8)
H_1-H_1'	2.75 (13)	C_4-N-C_6	111.7 (7)
$N-C_4$	1.52 (1)	C_5-N-C_6	109.0 (9)
$N-C_5$	1.44 (1)	C_6-N-C_6'	103.7 (16)
$N-C_6$	1.44 (1)		

[a] The standard deviations of the least significant figures are given in parentheses.

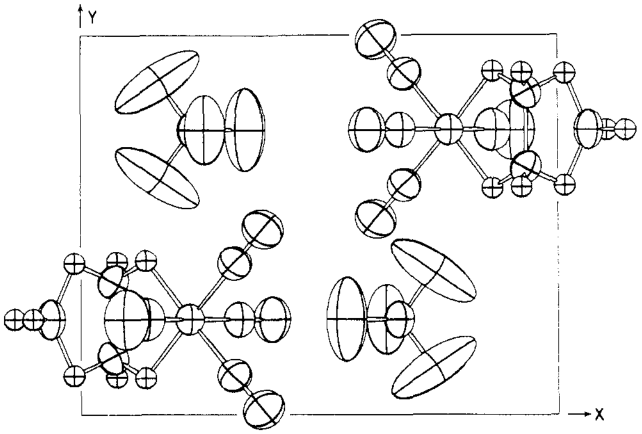

Figure 2.—The *xy* projection of a portion of the crystal structure of $[(CH_3)_4N][(CO)_4CrB_3H_8]$.

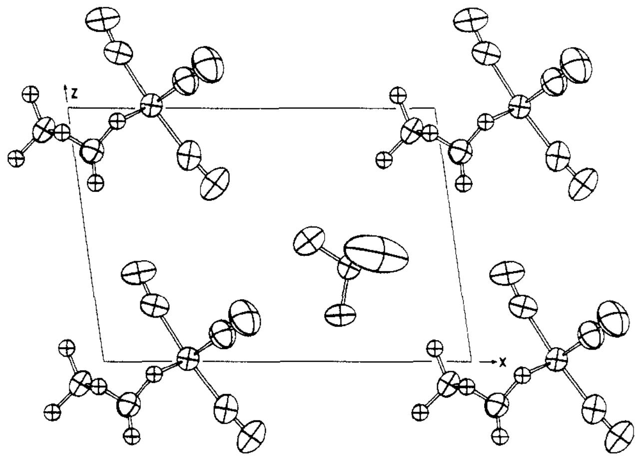

Figure 3.—The *xz* projection of a portion of the crystal structure of $[(CH_3)_4N][(CO)_4CrB_3H_8]$. There is another layer of ions in the cell related to these by the 2_1 axis.

$B_3H_8^-$ ion.[25] The observed B–B distances in the $B_3H_8^-$ ion are 1.77 and 1.80 Å for B_1-B_2 and B_2-B_2', respectively, while the observed terminal B–H distances varied from 1.05 to 1.20 Å. Approximate bridging B–H distances of 1.5 Å for B_1-H_3 and 1.2 Å for B_2-H_3 were found in the $B_3H_8^-$ structure. Clearly the B_3H_8 geometry in $B_3H_8^-$ is very similar to that found here for $(CO)_4CrB_3H_8^-$. In the $B_3H_8^-$ structure it appeared that the bridging hydrogen atom positions were disordered. There was no evidence for such disorder in this structure; the isotropic temperature factor for H_3 refined to 3.2 Å^2 in an intermediate refinement cycle when the hydrogen thermal parameters were refined. The B–B and B–H distances found in $(CO)_4CrB_3H_8^-$ are similar to those observed in related compounds.[26] The B_1-H_3 distance of 1.43 Å is a little long, but then the B–H bridging distances must accommodate the hybridizations of B_2 and B_2'. A similar bonding situation occurs in B_4H_{10}[27] where the distance is also 1.43 Å.

The *xy* projection of a portion of the crystal structure is shown in Figure 2. A portion of the structure in the *xz* projection is shown in Figure 3. Figure 3 in particular illustrates the compromise made between the atom hybridizations and the intramolecular repulsions. The dihedral angle between the plane of the three boron atoms and the plane defined by the Cr atom and the two equatorial C's is 59.7°. All contacts between ions were examined. The shortest nonhydrogen atom contact is 3.33 Å between O_1 and C_5 $(x, y, z - 1)$. The shortest hydrogen to nonhydrogen distance is 3.01 Å between H_2 and C_6 $(1 - x, 1 - y, -z)$. The shortest contacts between hydrogen atoms are 2.53 and 3.11 Å between H_1 and H_3 $(-x, 1 - y, -z)$ and H_5 $(-x, 1 - y, -z)$, respectively. The large anisotropic thermal parameters of the carbon atoms of the tetramethylammonium ions are evident in Figures 2 and 3. The thermal parameters of the carbon atoms appear to be too large to result merely from librational motion of the cation. There is probably also some static disorder in the cation positions wherein individual cations occur at positions in the cell rotated slightly from the average position.

The bonding in this compound can be described fairly well in the valence-bond language in terms of localized bonds with three-center, two-electron Cr–H–B bonds linking the B_3H_8 moiety to the Cr atom. The Cr atom achieves a rare-gas electron configuration in this interpretation. Such a simple interpretation, however, does not give any insight into structural details such as the differences in equatorial and axial Cr–C distances.

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Bonding in $(CO)_4CrB_3H_8^-$

Calculations of the LCAO–MO extended-Hückel variety[28] were performed on the $(CO)_4CrB_3H_8^-$ configuration to examine the bonding implications of some of the observed structural parameters. In particular, the question arises as to the reason for the observed differences in the equatorial and axial Cr–CO distances. The axial Cr–CO distances in this structure are about 0.08 Å longer than the equatorial ones. This difference is certainly significant in view of the errors involved (Table IV).

The refined atom positions determined in this work were used in the molecular orbital calculations. The basis set consisted of 9 chromium (3d, 4s, 4p), 16 carbon (2s, 2p), 16 oxygen (2s, 2p), 12 boron (2s, 2p), and 8 hydrogen (1s) atomic orbitals. The chromium (4s and 4p), carbon, and oxygen orbital exponents used were those obtained by Carroll and McGlynn[29] by matching single Slater-type functions with many-term SCF functions. The boron and hydrogen exponents were those used in earlier calculations on boranes.[30] The "double-ζ" form of the Cr 3d orbitals was used.[31] The Coulomb integrals were taken as the negative of the valence-state ionization potentials (VSIP). The carbon and oxygen H_{ii} terms were taken from Cusachs and Reynolds.[32] The Cr H_{ii} terms were evaluated as a function of charge and electronic configuration.[33] The Cr orbital energies were varied in a self-consistent-charge iterative procedure. These data are summarized in Table V. The off-diagonal matrix elements were evaluated using the Wolfsberg–Helmholz[34] approximation of $H_{ij} = KS_{ij}(H_{ii} + H_{jj})/2$ with $K = 1.75$.

TABLE V

ORBITAL EXPONENTS AND ENERGIES

Atom	Orbital	Exponent	$-H_{ii}$, eV
Chromium	3d	4.95 (0.4876)[b] 1.60 (0.7205)	11.07[a]
Chromium	4s	1.31	10.47
Chromium	4p	0.77	7.37
Oxygen	2s (1s)[c]	1.42	32.00
Oxygen	2p (1p)	1.23	15.30
Carbon	2s (1s)	1.02	21.20
Carbon	2p (2p)	1.42	11.40
Boron	2s	1.29	14.90
Boron	2p	1.21	8.42
Hydrogen	1s	1.00	13.60

[a] The energies of the chromium atomic orbitals are the values at the end of the iterative procedure. [b] The numbers in parentheses are the coefficients in the "double-ζ" expansion. [c] The orbitals in parentheses are the overlap-matched orbitals; the exponents for oxygen and carbon are for these orbitals.

This calculation resulted in a $^1A'$ ground state with a gap energy of 3.62 eV between the highest occupied and lowest unoccupied molecular orbitals. The net charge on the chromium atom was −0.12 eV with the resultant configuration $(3d)^{5.98}(4s)^{0.12}(4p)^{0.02}$. The Cr charge does not seem unreasonable especially since the ion carries a negative charge. The atom charges for the other atoms are as follows: C_1 (0.60), O_1 (−0.66), C_2 (0.63), O_2 (−0.64), C_3 (0.62), O_3 (−0.76), B_1 (0.31), B_2 (0.01), H_1 (−0.05), H_2 (−0.19), H_3 (0.02), H_4 (−0.21), H_5 (−0.18). Of course, the charges for the symmetry-related atoms are equivalent. The charges on the CO groups are somewhat high in view of what one might expect for the partial Cr–CO dipole moment. These charges could be lowered by altering these orbital exponents as a function of charge. Such a refined procedure would change the quantitative features of the results; however, both equatorial and axial CO's would be influenced similarly and the qualitative features of this calculation would not be altered significantly. The unique boron with two terminal hydrogen atoms attached is clearly the more positive of the two types of boron atoms. The difference in charge here is similar to that calculated by Lipscomb[26] for the isolated $B_3H_8^-$ ion where the charges for B_1 and B_2 are 0.12 and −0.16, respectively.

Interesting insights into the nature of the Cr–CO bonding are obtained if the Mulliken overlap population is used as an indication of the strength of the covalent interaction between atoms. A comparison of the overlap populations and their breakdown into σ and π contributions are given in Table VI. The usual conception of metal–carbonyl bonding involves σ donation from the carbonyl group to the metal atom and simultaneous π back-donation from the metal atom to the carbonyl group. In this calculation the σ donation is the same for both the equatorial and axial Cr–C interactions. However, the π back-donation is 28% larger for the equatorial Cr–C bonds. As expected, the differences in Cr–C overlaps are matched inversely by the carbonyl C–O overlaps.

TABLE VI

OVERLAP POPULATIONS FOR CHROMIUM–CARBONYL INTERACTIONS

Interaction	Overlap population	Obsd distance, Å
Cr–C(equatorial)	σ 0.318	1.824
	π 0.375	
	0.693	
Cr–C(axial)	σ 0.315	1.900
	π 0.294	
	0.609	
C–O(equatorial)	1.310	1.16
C–O(axial)	1.415	1.13

In this calculation the π back-donation is slightly less than the σ donation for the axial Cr–C bonds but considerably greater for the equatorial Cr–C bonds. In calculations on $Cr(CO)_6$ and $C_6H_6Cr(CO)_3$[29] the π back-donation was also found to be larger than the σ donation. The actual numbers involved here certainly depend somewhat on the parameterization used

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in the calculation. However, the variations in σ and π bonding within a given molecule would not be expected to be nearly as sensitive to parameterization. A separate calculation was done adjusting the equatorial lengths to 1.900 Å for Cr–C and 1.13 Å for C–O to match the axial distances with the expectation that the only significant effect would be in the equatorial Cr–C π bonding. This was confirmed; the Cr–C σ contributions were again nearly equal (0.326 equatorial and 0.321 axial) but the equatorial π contribution was reduced to 0.327, still slightly greater than the axial π contribution of 0.304. Thus, the only significant difference on forcing equivalent equatorial and axial bond lengths was a decrease in the equatorial Cr–C π bonding. The implication is that in $(CO)_4CrB_3H_8^-$ the 0.08-Å difference between axial and equatorial Cr–C distances results from increased π bonding in the equatorial Cr–C bonds. As the Cr–C overlap increases, the C–O overlap decreases; this, too, is reflected in the observed carbonyl C–O distances.

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Metal Carbonyl–Trifluorophosphine Systems. VIII. Spectral Studies and the Fluxional Nature of Butadienetricarbonyliron(0)

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Butadienetricarbonyliron(0) undergoes photochemical or thermal exchange with ^{13}CO and substitution with PF_3. Very little butadiene replacement occurs. Cotton–Kraihanzel type force constant calculations have been made on the $C_4H_6Fe(CO)_x(PF_3)_{3-x}$ species. The carbonyl force constants for the tricarbonyl have been determined and these constants can be used to calculate all ^{13}CO frequencies. Those up through dicarbonyl-^{13}C have been verified by isotopic enrichment. The tricarbonyl moiety has one unique carbonyl position which is occupied by PF_3 on substitution. Low-temperature fluorine nmr confirms the nonequivalence of the three positions in $C_4H_6Fe(CO)(PF_3)_2$. At room temperature, the nmr spectra of $C_4H_6Fe(CO)(PF_3)_2$ and $C_4H_6Fe(PF_3)_3$ show a time-averaged equivalence indicating some form of fluxional nature in the structure. It is suggested that this is a rotational motion comparable to the Bailar twist.

Introduction

Butadienetricarbonyliron(0), $C_4H_6Fe(CO)_3$, is one of the earlier known organometallic compounds,[1,2] yet its spectral properties and substitution reactions have received only limited attention.

The tricarbonyl was reported by Pauson[2] to have two stretching vibrations in the carbonyl region. This can lead to the assumption that the tricarbonyl portion possesses C_{3v} symmetry. This symmetry does not agree with the X-ray structure, however.[3] More recently, higher resolution infrared spectrometers have shown the presence of three carbonyl vibrations rather than two[4] indicating that the symmetry is indeed lower than C_{3v}.

Only limited studies have been made concerning the reactions of $C_4H_6Fe(CO)_3$ with neutral ligands. In these reactions, either the diene or the carbonyl groups can be replaced. Both reactions have been observed. For instance, it has been reported that triphenylphosphine reacts thermally with $C_4H_6Fe(CO)_3$ to yield $Fe(CO)_2[P(C_6H_5)_3]_3$[5] whereas photochemically these compounds react to yield $C_4H_6Fe(CO)_2P(C_6H_5)_3$, $C_4H_6Fe(CO)[P(C_6H_5)_3]_2$, $Fe(CO)_3[P(C_6H_5)_3]_2$, and an unidentified red product.[6]

To further the understanding of $C_4H_6Fe(CO)_3$, additional studies have been undertaken. These studies include detailed force constant calculations on the tricarbonyl utilizing its ^{13}CO-enriched analogs. They also include a study of the reaction products of $C_4H_6Fe(CO)_3$ with PF_3 and a subsequent proton and fluorine nmr investigation of the resulting $C_4H_6Fe(CO)_x(PF_3)_{3-x}$ products.

The use of phosphorus trifluoride as a ligand was particularly revealing. Past studies[7] have shown that PF_3 and CO are so similar as ligands that they substitute quite freely for one another with very little change in either the physical properties or the bonding. However, PF_3 is quite amenable to nmr study whereas carbonyl groups are not.

From these studies have come an unexpected example of a fluxional compound.

Experimental Section

Butadieneiron tricarbonyl was obtained from Alfa Inorganics. It was sufficiently pure to be used as received or as it was after simple vacuum distillation. Its properties were unchanged upon gas–liquid partition chromatographic purification.

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