to be "averaged away" by the factor $N^{1/2}$. The value of $\sigma(F^2_{av})$ was further *increased* by a factor of $\{[\sum(F^2 - F^2_{av})/\sigma^2(F^2)]/(N-1)\}^{1/2}$ if that quantity was >1.0. (N = number of F^2 values averaged.)

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Crystal Structure and Molecular Geometry of $Ir(B_5H_8)Br_2(CO)(PMe_3)_2$, a Product from the Oxidative Addition of Bromopentaborane to $IrCl(CO)(PMe_3)_2$, and Some Comments on the Structural Trans Influence of σ-Bonded Boron

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The complex $Ir(B_5H_8)Br_2(CO)(PMe_3)_2$, a product from the oxidative addition of (1- or 2-) BrB_5H_8 to $IrCl(CO)(PMe_3)_2$, has been examined by a single-crystal X-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] with a = 13.824 (4) Å, b = 10.661 (3) Å, c = 13.611 (3) Å, and β = 104.90 (2)°. Observed and calculated densities are ρ(obsd) = 2.012 and ρ(calcd) = 2.036 g cm^{-3} for mol wt 594.3 and Z = 4. X-Ray diffraction data complete to 2θ = 45° (Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer and the structure was solved via the use of Patterson, Fourier, and least-squares refinement techniques. All atoms other than the hydrogen atoms associated with the methyl groups have been located, the final discrepancy indices being R_F = 4.84% and R_{wF} = 4.88% for the 2558 independent reflections. The molecular geometry thus determined shows the complex to be *cis*-dibromo-*trans*-bis(trimethylphosphine)(2-pentaboranyl)carbonyliridium(III). The geometry about the central iridium(III) atom approximates to octahedral, with cis angles ranging from 86.19 (8) to 93.54 (36)° and trans angles from 172.17 (10) to 177.81 (38)°. The two iridium–phosphorus distances are 2.362 (3) and 2.361 (3) Å, while iridium–bromine distances are Ir–Br(1) = 2.638 (1) Å [trans to σ-bonded boron] and Ir–Br(2) = 2.516 (1) Å [trans to a carbonyl ligand]. σ-Bonded boron thus seems to exert a strong trans-lengthening effect, as does σ-bonded carbon in metal alkyls. The pentaboranyl ligand is bonded to iridium via its basal (2) position, with Ir–B(2) = 2.071 (14) Å. Distances within the square-pyramidal B_5H_8 moiety are as follows: B(apical)–B(basal) = 1.641 (21)–1.691 (18) Å, B(basal)–B(basal) = 1.805 (20)–1.912 (18) Å, B–H(terminal) = 1.08 (8)–1.55 (11) Å, and B–H(bridging) = 1.03 (14)–1.45 (10) Å.

Introduction

The oxidative addition of boron halides and diphenylboron halides to $[(C_5H_5)_2Ti]_2$, $(diphos)_2Co$, and $(Ph_3P)_4Pt$ was reported some years ago.[1] Oxidative addition of boron–hydrogen bonds has been shown to lead to such species as $Ir(H)(Cl)[C_2B_{10}H_{10}PMe_2][C_2B_{10}H_{11}PMe_2]_2$[2] and 3-$[(PPh_3)_2Ir(H)Cl]$-1,2-$C_2B_{10}H_{11}$;[3] in addition to this, hydridometallocarboranes have been used as homogeneous catalysts[4] and deuterated boron hydrides have been prepared by transition metal catalyzed exchange of deuterium gas with terminal boron–hydrogen bonds.[5]

Recently, Davison and his coworkers[6] have studied the reaction of 1-BrB_5H_8 and 2-BrB_5H_8 with $IrCl(CO)(PMe_3)_2$ and found the identical product, $Ir(B_5H_8)Br_2(CO)(PMe_3)_2$, in each case. We have examined this product of oxidative addition and metathesis by means of a single-crystal X-ray structural analysis. A preliminary report of this work has appeared previously;[6] a full account appears below.

Collection of the X-Ray Diffraction Data

Yellow crystals of the complex were provided by Professor A. Davison of Massachusetts Institute of Technology. The crystal used for the diffraction study was needle shaped, being 0.63 mm in length (along [101]) and having a cross section of 0.175 mm × 0.191 mm. It was mounted along its extended [101] direction. Preliminary photographic studies, using Weissenberg, rotation, precession, and cone-axis techniques, revealed the approximate unit cell dimensions, showed C_{2h} ($2/m$) Laue symmetry, and indicated the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. These extinctions suggest that the crystal belongs to the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14].

The crystal was transferred to a Picker FACS-1 diffractometer, was accurately centered, and was aligned with [101] precisely coincident with the instrumental ϕ axis.

As a check on absorption, the intensity of the strong axial 202 reflection was measured at χ = 90° and at 10° intervals from ϕ = 0° to ϕ = 350°. The resulting variation in intensity as a function of ϕ [(maximum − minimum)/(average) = 29%] indicated that an absorption correction would be necessary. The "ϕ-scan" data were processed along with the primary data set; following correction for absorption the ϕ dependence of the 202 reflection was reduced to 3.5%, thus confirming the validity of the absorption correction.

Details of the data collection are provided in Table I; the apparatus and experimental technique have been described previously.[7]

We note here that the crystal was severely affected by X irradiation. The three check reflections decreased steadily during data collection—202 by 41%, $\bar{5}02$ by 23%, and 131 by 15%; all data were brought to a common scale by the use of an anisotropic linear-decay correction.[8]

Solution and Refinement of the Structure

Programs used in determining the structure include FORDAP (Fourier synthesis, by A. Zalkin), LSHF (structure factor calculations with full-matrix least-squares refinement, by B. G. DeBoer), STAN1 (distances and angles with their esd's, by B. G. DeBoer), PLOD (least-squares planes and lines, by B. G. DeBoer), and ORTEP (thermal

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Table I. Experimental Data for the X-Ray Diffraction Study

(A) Crystal Parameters at 23°

$a = 13.8237\ (36)$ Å Space group $P2_1/c$ [C_{2h}^5; No. 14]
$b = 10.6606\ (28)$ Å $Z = 4$
$c = 13.6112\ (34)$ Å Mol wt 594.305
$\beta = 104.90\ (2)°$ ρ(calcd) = 2.036 g cm^{-3}
$V = 1938.4$ Å^3 ρ(obsd) = 2.012 g cm^{-3} [13]

(B) Measurement of Intensity Data

Radiation: Mo Kα
Filter(s): Nb foil at counter aperture (~47% transmission of Mo Kα)
Attenuators: not used
Takeoff angle: 3.0°
Detector aperture: 3 mm × 4 mm (∥ and ⊥ to the diffraction plane)
Crystal–detector distance: 330 mm
Crystal orientation: aligned on [101]
Reflections measured: $\pm h, +k, +l$
Maximum 2θ: 45°
Scan type: coupled θ(crystal)–2θ(counter)
Scan speed: 1.0°/min
Scan length: $\Delta(2\theta) = (1.00 + 0.692 \tan \theta)°$, starting 0.50° below the Mo Kα_1 peak.
Background measurement: stationary crystal, stationary counter; 20 sec each at beginning and end of 2θ scan
Standard reflections: Three remeasured after every 48 reflections; rms deviations (after application of an anisotropic linear decay correction) were 2.58% for 202, 1.27% for 502, and 1.08% for 131
Reflections collected: 2558 independent measurements and 171 systematic absences

(C) Treatment of Intensity Data

Conversion to $|F_o|$ and $\sigma(|F_o|)$: as in ref 7, using "ignorance factor" of $p = 0.02$
Absorption coefficient: $\mu = 118.16$ cm^{-1}; maximum and minimum transmission factors were 0.198 and 0.136

ellipsoid drawings, by C. K. Johnson).

Scattering factors for neutral iridium, bromine, phosphorus, oxygen, carbon, and boron were taken from the compilation of Cromer and Waber;[9] both the real and imaginary components of anomalous dispersion were included for all nonhydrogen atoms, using the values of Cromer and Liberman.[10] For hydrogen, the scattering factors of Stewart et al.[11] were used.

The function minimized in least-squares refinement is $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(|F_o|)$. Discrepancy indices used below are defined as

$$R_F = \left[\frac{\Sigma \| F_o| - |F_c\|}{\Sigma |F_o|}\right] \times 100\ (\%)$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w |F_o|^2}\right]^{1/2} \times 100\ (\%)$$

The analysis was begun using data that had yet to be corrected for absorption. The positions of the iridium and two bromine atoms were quickly and unambiguously determined from a three-dimensional Patterson synthesis. A Fourier synthesis, phased by these three atoms, revealed the positions of the two PC_3 fragments and the CO ligand.

Five cycles of full-matrix least-squares refinement of the scale factor along with positional and isotropic thermal parameters of atoms in the $IrBr_2(CO)(PC_3)_2$ portion of the molecule (53 parameters) led to convergence with R_F = 11.00% and R_{wF} = 12.07%. A difference-Fourier synthesis now revealed the positions of the five boron atoms. Refinement of positional and anisotropic thermal parameters for all 18 nonhydrogen atoms, along with the scale factor (163 parameters), led to convergence with R_F = 6.42% and R_{wF} = 6.49%.

The absorption-corrected data were now introduced and a "β-filter correction" was applied to the low-angle data;[7] continued refinement led to convergence with R_F = 5.05% and R_{wF} = 5.28%. A difference Fourier calculated at this stage showed peaks of height 1.96, 1.61, and 1.09 e Å^{-3} very close to the position of the iridium atom; the eight hydrogen atoms of the B_5H_8 moiety were clearly visible, with peak heights ranging from 0.65 to 0.48 e Å^{-3}. A few hydrogen atoms on the PMe_3 ligands were also visible; however, it proved impossible to locate unequivocally sets of hydrogens about each of the six methyl carbon atoms, so hydrogen atoms of the methyl groups were not included in any subsequent calculations.

Table II. Final Positional and Isotropic Thermal Parameters[a,b]

Atom	x	y	z	B, Å^2
Ir	0.280572 (28)	0.046606 (35)	0.204126 (27)	3.35
Br(1)	0.44097 (10)	0.06041 (13)	0.13344 (11)	6.62
Br(2)	0.17076 (08)	0.15383 (11)	0.05097 (08)	5.24
P(1)	0.32198 (22)	0.25010 (27)	0.27015 (20)	4.45
P(2)	0.23550 (23)	−0.14410 (27)	0.11599 (22)	4.88
O(1)	0.39819 (71)	−0.07520 (91)	0.38486 (69)	6.19
C(1)	0.3615 (11)	−0.0356 (12)	0.3252 (11)	5.60
C(2)	0.4137 (11)	0.2547 (13)	0.3927 (09)	8.09
C(3)	0.2193 (11)	0.3447 (12)	0.2903 (11)	8.03
C(4)	0.3730 (09)	0.3500 (11)	0.1876 (09)	6.46
C(5)	0.2832 (10)	−0.2845 (11)	0.1937 (10)	7.50
C(6)	0.2846 (11)	−0.1573 (13)	0.0019 (09)	7.69
C(7)	0.1034 (09)	−0.1771 (11)	0.0659 (09)	6.16
B(1)	0.0920 (11)	−0.0765 (13)	0.3113 (10)	5.05
B(2)	0.1621 (11)	0.0321 (11)	0.2707 (09)	4.60
B(3)	0.0266 (11)	0.0285 (16)	0.2338 (11)	5.85
B(4)	0.0168 (11)	0.0108 (15)	0.3635 (12)	6.28
B(5)	0.1515 (11)	0.0179 (13)	0.4076 (10)	5.35
H(1)	0.0827 (62)	−0.1766 (83)	0.2987 (63)	4.3 (20)
H(3)	−0.0349 (79)	0.0067 (96)	0.1685 (81)	5.7 (26)
H(4)	−0.0361 (81)	−0.0530 (95)	0.4376 (82)	9.5 (31)
H(5)	0.2107 (61)	0.0000 (77)	0.4872 (63)	3.6 (18)
HB(1)	0.1042 (61)	0.1130 (79)	0.2359 (62)	3.3 (18)
HB(2)	−0.0150 (73)	0.0981 (91)	0.2805 (79)	5.6 (24)
HB(3)	0.0651 (97)	0.0850 (98)	0.3851 (96)	5.0 (25)
HB(4)	0.1641 (71)	0.1005 (98)	0.3267 (77)	5.7 (26)

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit of the preceding number. [b] Equivalent isotropic thermal parameters are given for nonhydrogen atoms. For anisotropic thermal parameters, see Table III.

Four cycles of full-matrix least-squares refinement of the scale factor, positional parameters for the 26 atoms in the $Ir(B_5H_8)Br_2(CO)(PC_3)_2$ portion of the molecule, anisotropic thermal parameters for the 18 nonhydrogen atoms, and isotropic thermal parameters for the 8 boranyl hydrogen atoms (195 parameters in all) led to final convergence ($\Delta/\sigma < 0.2$ for all parameters) with R_F = 4.84% and R_{wF} = 4.88% for all 2558 reflections and R_F = 4.64% and R_{wF} = 4.25% for the 2546 reflections for which $|\Delta F|/\sigma(|F_o|) < 10.0$. [Note that no reflections were omitted from the analysis on the basis of being "not significantly above background".]

The standard deviation in an observation of unit weight or "goodness of fit", defined by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.672, where the number of reflections (m) was 2546 and the number of refined parameters (n) was 195. The ratio of observations to parameters was $m{:}n$ = 13.0:1. The function $\sum w(|F_o| - |F_c|)^2$ was not significantly dependent either upon $|F_o|$ or upon $((\sin \theta)/\lambda)$, thereby suggesting that the weighting scheme was satisfactory. Evidence for extinction was sought; none was found.

The correctness of the determined structure was confirmed by means of a final difference-Fourier synthesis. The three most significant peaks (of height 1.95, 1.61, and 1.08 e Å^{-3}) were close to (i.e., within 1 Å of) the position of the iridium atom; all other features were less than 0.75 e Å^{-3} in height.

A table of observed and calculated structure factor amplitudes is available.[12] Positional parameters and their estimated standard deviations (esd's) are given in Table II. Anisotropic thermal parameters are collected in Table III.

The Molecular Structure

The overall stereochemistry and the labeling of all nonhydrogen atoms in the $Ir(2\text{-}B_5H_8)Br_2(CO)(PMe_3)_2$ molecule are shown in Figure 1. Interatomic distances and their estimated standard deviations (esd's) are listed in Table IV; interatomic angles and their esd's are shown in Table V.

The molecule is formed by the oxidative addition of 1-BrB_5H_8 or 2-BrB_5H_8 to $IrCl(CO)(PMe_3)_2$. Subsequent or simultaneous halide metathesis, yielding the dibromo derivative,[13] unfortunately leads to our being unable to determine

Table III. Anisotropic Thermal Parameters[a,b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle$[c]
Ir	3.849 (20)	3.030 (18)	2.981 (19)	0.154 (16)	0.529 (13)	0.138 (15)	0.19, 0.20, 0.23
Br(1)	6.65 (7)	6.57 (7)	7.24 (7)	0.97 (6)	2.87 (6)	0.74 (6)	0.26, 0.28, 0.33
Br(2)	5.78 (6)	5.32 (6)	4.02 (5)	0.51 (5)	0.23 (4)	0.77 (5)	0.21, 0.27, 0.29
P(1)	5.68 (15)	3.9 (1)	3.7 (1)	−0.8 (1)	1.1 (1)	−0.3 (1)	0.21, 0.22, 0.28
P(2)	6.0 (2)	3.7 (1)	4.6 (1)	0.2 (1)	0.7 (1)	−0.4 (1)	0.21, 0.24, 0.29
O(1)	6.2 (5)	6.2 (5)	5.8 (5)	0.7 (4)	0.6 (4)	1.1 (4)	0.24, 0.30, 0.30
C(1)	6.3 (8)	4.3 (7)	7.5 (8)	−1.4 (6)	4.1 (7)	−2.4 (6)	0.19, 0.22, 0.35
C(2)	10.3 (9)	6.9 (7)	5.2 (6)	−2.6 (7)	−1.4 (6)	−0.8 (6)	0.21, 0.30, 0.42
C(3)	11.0 (10)	4.3 (6)	10.7 (10)	0.9 (6)	6.2 (8)	−0.7 (6)	0.21, 0.30, 0.41
C(4)	9.2 (8)	4.8 (6)	6.1 (6)	−2.6 (6)	3.4 (6)	−0.0 (5)	0.20, 0.27, 0.36
C(5)	9.8 (9)	3.9 (6)	7.8 (8)	2.3 (6)	0.4 (7)	0.7 (5)	0.20, 0.31, 0.39
C(6)	10.9 (9)	7.4 (8)	5.9 (7)	−0.8 (7)	4.1 (7)	−2.4 (6)	0.21, 0.32, 0.38
C(7)	6.4 (6)	5.1 (6)	6.2 (6)	−1.3 (5)	0.3 (5)	−1.2 (5)	0.21, 0.29, 0.32
B(1)	5.9 (7)	4.8 (7)	4.5 (6)	−0.9 (6)	1.5 (6)	−0.0 (5)	0.23, 0.24, 0.29
B(2)	6.9 (8)	3.4 (6)	3.0 (5)	0.7 (5)	0.3 (5)	−0.5 (5)	0.18, 0.21, 0.31
B(3)	5.1 (7)	8.4 (10)	4.3 (6)	−0.2 (7)	1.5 (6)	−0.2 (7)	0.23, 0.25, 0.33
B(4)	4.9 (7)	7.3 (8)	6.8 (8)	−2.1 (6)	2.0 (6)	−0.2 (7)	0.21, 0.29, 0.33
B(5)	5.6 (7)	5.9 (7)	4.9 (7)	−0.7 (6)	2.1 (6)	0.9 (6)	0.21, 0.27, 0.29

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameters and have units of Å². They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] See footnote *a* to Table II. [c] These values correspond to the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see the figures.

Table IV. Interatomic Distances (Å) with Esd's

Atoms	Dist	Atoms	Dist
(A) Distances from Iridium Atom			
Ir-Br(1)	2.6384 (14)	Ir-B(2)	2.071 (14)
Ir-Br(2)	2.5158 (12)	Ir-C(1)	1.946 (17)
Ir-P(1)	2.3616 (28)	Ir···O(1)	2.885 (9)
Ir-P(2)	2.3614 (29)	Ir···HB(1)	2.68 (8)
		Ir···HB(4)	2.66 (10)
(B) Phosphorus-Carbon Bond Lengths			
P(1)-C(2)	1.818 (12)	P(2)-C(5)	1.854 (11)
P(1)-C(3)	1.819 (12)	P(2)-C(6)	1.853 (11)
P(1)-C(4)	1.817 (10)	P(2)-C(7)	1.812 (12)
(C) Carbon-Oxygen Distance			
C(1)-O(1)	0.939 (15)		
(D) Boron-Boron Distances			
B(1)-B(2)	1.691 (18)	B(2)-B(3)	1.811 (20)
B(1)-B(3)	1.641 (21)	B(2)-B(5)	1.912 (18)
B(1)-B(4)	1.683 (21)	B(3)-B(4)	1.815 (20)
B(1)-B(5)	1.688 (19)	B(4)-B(5)	1.805 (20)
(E) Boron-(Terminal Hydrogen) Distances			
B(1)-H(1)	1.08 (8)	B(4)-H(4)	1.55 (11)
B(3)-H(3)	1.08 (11)	B(5)-H(5)	1.19 (8)
(F) Boron-(Bridging Hydrogen) Distances			
B(2)-HB(1)	1.19 (8)	B(4)-HB(3)	1.03 (14)
B(3)-HB(1)	1.40 (8)	B(5)-HB(3)	1.36 (15)
B(3)-HB(2)	1.21 (10)	B(5)-HB(4)	1.05 (10)
B(4)-HB(2)	1.44 (10)	B(2)-HB(4)	1.45 (10)

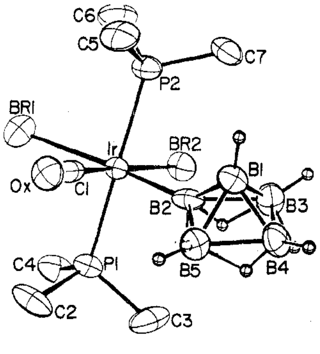

Figure 1. General view of the $Ir(2\text{-}B_5H_8)Br_2(CO)(PMe_3)_2$ molecule, showing the labeling of atoms [ORTEP diagram; 50% probability ellipsoids for nonhydrogen atoms and with hydrogen atoms represented by spheres of radius 0.1 A].

Table V. Interatomic Angles (deg) with Esd's

Atoms	Angle	Atoms	Angle
(A) Angles around the Iridium Atom			
Br(1)-Ir-Br(2)	93.28 (4)	Br(2)-Ir-B(1)	91.14 (34)
Br(1)-Ir-P(1)	86.75 (8)	P(1)-Ir-P(2)	172.17 (10)
Br(1)-Ir-P(2)	89.97 (8)	P(1)-Ir-C(1)	93.50 (36)
Br(1)-Ir-C(1)	88.87 (35)	P(1)-Ir-B(1)	92.52 (34)
Br(1)-Ir-B(2)	175.46 (35)	P(2)-Ir-C(1)	93.54 (36)
Br(2)-Ir-P(1)	86.19 (8)	P(2)-Ir-B(1)	91.30 (34)
Br(2)-Ir-P(2)	86.91 (8)	C(1)-Ir-B(1)	86.70 (48)
Br(2)-Ir-C(1)	177.81 (38)		
(B) Iridium-Phosphorus-Carbon Angles			
Ir-P(1)-C(2)	114.67 (46)	Ir-P(2)-C(5)	113.36 (42)
Ir-P(1)-C(3)	116.41 (46)	Ir-P(2)-C(6)	112.67 (45)
Ir-P(1)-C(4)	113.45 (39)	Ir-P(2)-C(7)	117.83 (39)
(C) Carbon-Phosphorus-Carbon Angles			
C(2)-P(1)-C(3)	103.54 (70)	C(5)-P(2)-C(6)	105.28 (64)
C(3)-P(1)-C(4)	102.12 (62)	C(6)-P(2)-C(7)	102.77 (60)
C(4)-P(1)-C(2)	105.16 (60)	C(7)-P(2)-C(5)	103.56 (59)
(D) Iridium-Carbon-Oxygen Angle			
Ir-C(1)-O(1)	177.6 (12)		
(E) Iridium-Boron-Boron Angles			
Ir-B(2)-B(1)	141.1 (9)	Ir-B(2)-B(5)	134.4 (8)
Ir-B(2)-B(3)	139.3 (8)		
(F) Boron-Boron-Boron Angles			
B(2)-B(1)-B(3)	65.8 (8)	B(1)-B(3)-B(2)	58.4 (8)
B(2)-B(1)-B(4)	103.2 (10)	B(1)-B(3)-B(4)	58.0 (8)
B(2)-B(1)-B(5)	68.9 (8)	B(2)-B(3)-B(4)	93.6 (9)
B(3)-B(1)-B(4)	66.2 (9)	B(1)-B(4)-B(3)	55.8 (8)
B(3)-B(1)-B(5)	99.8 (11)	B(1)-B(4)-B(5)	57.7 (8)
B(4)-B(1)-B(5)	64.8 (8)	B(3)-B(4)-B(5)	89.5 (9)
B(1)-B(2)-B(3)	55.8 (8)	B(1)-B(5)-B(2)	55.6 (7)
B(1)-B(2)-B(5)	55.5 (7)	B(1)-B(5)-B(4)	57.5 (8)
B(3)-B(2)-B(5)	86.3 (8)	B(2)-B(5)-B(4)	90.6 (9)
(G) Boron-(Bridging Hydrogen)-Boron Angles			
B(2)-HB(1)-B(3)	79 (4)	B(4)-HB(3)-B(4)	97 (8)
B(3)-HB(2)-B(4)	86 (6)	B(4)-HB(4)-B(1)	98 (8)

directly the stereochemistry of oxidative addition.

The molecule is an octahedral derivative of iridium(III) in which the two bromide ligands are mutually cis [Br(1)-Ir-Br(2) = 93.28 (4)°] and the two trimethylphosphine ligands are mutually trans [P(1)-Ir-P(2) = 172.17 (10)°]; the remaining ligands are a mutually cis carbonyl and a 2-pentaboranyl residue.

The two bromide ligands are decidedly nonequivalent. That trans to the carbonyl ligand [Br(2)-Ir-C(1) = 177.81 (38)°] is associated with a bond length of Ir-Br(2) = 2.5158 (12) Å. Insofar as we can tell, this seems to be a perfectly normal iridium-bromine distance. Thus, one would predict an Ir^{III}-Br distance of ca. 2.50–2.53 Å based upon the accepted covalent radii of ca. 1.36–1.39 Å for Ir(III)[14] and 1.14 Å for bromine.[15] While few studies of iridium–bromide species have been reported, the Ir–Br distance in $IrBr(CO)(TCNE)(PPh_3)_2$ is found to be 2.508 (2) Å.[16]

In sharp contrast to this, the Ir–Br(1) distance [trans to the σ-B_5H_8 ligand] is increased to a value of 2.6384 (14) Å. This must be the result of σ-bonded boron exerting a stronger trans-lengthening influence on a bromide ligand than does a carbonyl ligand. σ-Bonded boron thus appears to have a trans-lengthening influence analogous to, but even stronger than, σ-bonded carbon.

The two independent, chemically equivalent, and mutually trans iridium–phosphorus distances are Ir–P(1) = 2.3616 (28) Å and Ir–P(2) = 2.3614 (29) Å. These values are close to the center of the range of iridium–phosphorus distances [2.248 (8)–2.452 (9) Å] listed in the compilation of Churchill and Bezman.[17]

Distances and angles determined for the Ir–C(1)–O(1) system are Ir–C(1) = 1.946 (17) Å, C(1)–O(1) = 0.939 (15) Å, and Ir–C(1)–O(1) = 177.6(12)°. It seems highly probable that the carbon–oxygen and iridium–carbon distances are systematically in error, although the reason for this has not been established unequivocally. (However, see below.) A normal carbon–oxygen distance in a transition metal complex with terminal carbonyl ligands is in the range 1.13–1.16 Å, as opposed to the present value of 0.939 (15) Å. Characteristic values for an iridium–carbonyl linkage are 1.70 (5) Å in $[IrI(CO)(NO)(PPh_3)_2][BF_4]$,[18] 1.84 (4) Å in $IrCl(CN)(NCS)(CO)(PPh_3)_2$,[19] 1.858 (14) Å in $[IrCl(CO)(NO)(PPh_3)_2][BF_4]$,[20] and 1.873 (11) Å in $Ir(NO)(CO)(PPh_3)_2$[21] (cf. 1.946 (17) Å in the present complex).

The most reasonable explanation for the systematic pattern of errors in distances within the present Ir–C(1)–O(1) system is that there is disorder of the carbonyl ligand and some other ligand (presumably a bromide ligand). We have no direct evidence for this—there is no significant residual between the carbon and oxygen atom on the final difference-Fourier map, and the carbonyl ligand appears normal on a difference-Fourier map based on contributions from all atoms other than those in this ligand. However, the extension of the thermal vibration ellipsoid of C(1) along the Ir···O(1) direction is consistent with our hypothesis.

Using the idealized values $Ir–CO_{ideal}$ = 1.85 Å and $Ir–Br_{ideal}$ = 2.50 Å and the observed value Ir–C(1) = 1.97 Å and making the assumption that the observed position of C(1) represents the weighted average of disordered carbon and bromine atoms,[22] one can estimate the degree of disorder in the following way. Let the real occupancy of carbon at 1.85 Å from the iridium atom be $1 - \delta$ and the occupancy of bromine at 2.50 Å from the iridium (and 0.65 Å from the carbon) be δ. We then can set up the equation

$$[(1 - \delta)Z(\mathrm{C})][\text{Ir-CO}_{\text{ideal}}] + [(\delta)Z(\mathrm{Br})][\text{Ir-Br}_{\text{ideal}}] = [Z(\text{“composite atom”})][\text{Ir-C(1)}_{\text{obsd}}]$$

But

$$Z(\text{“composite atom”}) = (1 - \delta)Z(\mathrm{C}) + (\delta)Z(\mathrm{Br})$$

Substituting numerical values

$$(1 - \delta)(6)(1.85) + (\delta)(35)(2.50) = [(1 - \delta)(6) + (\delta)(35)](1.97)$$

whence $\delta = 0.037$.

Our observed lengthened Ir–C(1) bond distance can thus be explained as the result of a 96.3%:3.7% disorder of C(1)–O(1) and Br(1). Note that the contribution of Br(1) to the C(1)–O(1) ligand would represent only 3.7% of 35 electrons or ca. 1.3 e. This would not necessarily be observable under normal circumstances. The small occupancy of CO around the position principally occupied by Br(1) would be even less significant—3.7% of a carbon atom corresponds to 0.22 e and 3.7% of an oxygen atom corresponds to 0.30 e.

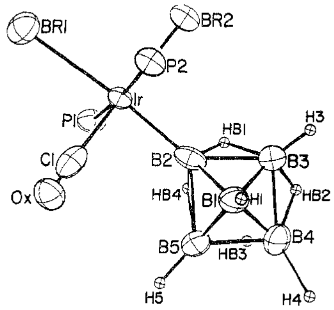

Figure 2. The $Ir(2\text{-}B_5H_8)Br_2(CO)(PMe_3)_2$ molecule, projected onto the basal plane of the pentaboranyl fragment and showing the labeling of hydrogen atoms [ORTEP diagram; conditions as for Figure 1].

Confidence in the reality of our suggested pattern of disorder is heightened significantly by previous observations of disorder in iridium–carbonyl–halide species. Thus Cl and CO are disordered in $IrCl(CN)(NCS)(CO)(PPh_3)_2$,[19] Cl and CO are disordered in $IrCl(CO)_2(PPh_3)_2$,[23] and I and CO are disordered in $Ir(O_2)I(CO)(PPh_3)_2$.[24]

The 2-Pentaboranyl Ligand

The pentaboranyl ligand is bonded to iridium via its basal (2) position, the iridium–boron bond distance being 2.071 (14) Å—slightly shorter than the reported Ir^{III}–C(sp^3) distances of 2.16 (2) Å in $(PhCHCH_2COPh)IrCl_2(Me_2SO)_2$[25] and 2.10 Å in $[Ir(CO)_2Cl(Me)]_2$.[26]

The boron framework of the B_5H_8 ligand defines a square pyramid in which B(1)–B(basal) distances range from 1.641 (21) to 1.691 (18) Å and B(basal)–B(basal) distances range from 1.805 (20) to 1.912 (18) Å. For comparison, we may note that the boron–boron distances in the parent boron hydride, B_5H_9, are B(apical)–B(basal) = 1.66 (2) Å and B(basal)–B(basal) = 1.77 (2) Å.[27,28] Angles within the boron framework are as follows: *cis*-B(basal)–B(apical)–B(basal) = 64.8 (8)–68.9 (8)°, *trans*-B(basal)–B(apical)–B(basal) = 99.8 (11)–103.2 (10)°, B(apical)–B(basal)–B(basal) = 55.5 (7)–58.4 (8)°, and B(basal)–B(basal)–B(basal) = 86.3 (8)–93.6 (9)°.

The precision with which hydride ligands have been located is low, with esd's on boron–hydrogen bond lengths ranging from 0.08 to 0.15 Å. However, the results of refinement do establish that the B_5H_8 ligand has the same topology as the B_5H_9 molecule—i.e., there are apical hydrogens (or, in the case of B(2), a complex iridium substituent) on each boron atom and there are bridging hydride ligands between each pair of adjacent boron atoms on the square base of the ligand (see Figure 2).

Individual boron–hydrogen distances are in the following ranges: B–H(apical) = 1.08 (8)–1.55 (11) Å and B–H(bridging) = 1.03 (14)–1.45 (10) Å. The B–H–B angles range from 79 (4) to 98 (8)°.

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Registry No. $Ir(B_5H_8)Br_2(CO)(PMe_3)_2$, 53221-42-4.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC408289-9-75.

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(13) The identity of this species as a dibromo derivative, rather than as a monobromomonochloro derivative was checked very carefully. (i) Elemental analysis of this sample is as follows (cf. ref 6). Anal. Calcd for the empirical formula $C_7H_{26}B_5Br_2IrOP_2$: C, 14.15; H, 4.42; B, 9.09; Br, 26.89; Ir, 32.34; P, 10.50. Found: C, 14.09; H, 4.39; B, 8.84; Br, 26.88; Ir, 35.45; P, 10.50. (ii) Based on the unit cell volume, the calculated density is 2.036 g cm^{-3} for the dibromo derivative and 1.884 g cm^{-3} for the monobromomonochloro derivative. We measured the density by "neutral buoyancy" in three different solutions, obtaining the following values: 2.014 g cm^{-3} for aqueous $ZnBr_2$, 2.015 g cm^{-3} for $C_2H_2Br_4$–CCl_4, and 2.008 g cm^{-3} for $C_2H_2Br_4$–$C_2H_4Cl_2$. The mean of these three values is 2.012 g cm^{-3}. Assuming *no* errors, this is consistent with there being a mixture of 84.2% dibromo and 15.8% monobromomonochloro complex. (iii) The behavior of the bromine atoms under least-squares refinement is reasonable. Br(1) is further distant from the iridium atom and has a higher thermal parameter than does B(2). An opposite effect would be expected if one atomic position were a composite "bromine–chlorine" atom. The centroid would then be closer to iridium that a normal bromine, and the thermal parameter should be higher than normal, reflecting (a) disorder about two atomic centers (a normal Cl position and a normal Br position) and (b) an electron count less than that expected for a pure bromine atom. We conclude, therefore, that, if the sample is contaminated by chloride, it is at a lower level than we can detect from an X-ray study.
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Determination of the Crystal Structure and Molecular Geometry of [Hydrotris(1-pyrazolyl)borato]copper(I) Carbonyl. A Unique Structural Investigation of a Copper–Carbonyl Linkage

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The species [hydridotris(1-pyrazolyl)borato]copper(I) carbonyl, $[HB(C_3N_2H_3)_3]Cu(CO)$, crystallizes in the noncentrosymmetric rhombohedral space group $R3c$ [C_{3v}^6; No. 161] with $a = 13.8616$ (21) Å and $\alpha = 91.37$ (1)°. The observed density is 1.45 (5) g cm^{-3}; that calculated for mol wt 304.58, $V = 2661.1$ (12) Å^3, and $Z = 8$ is 1.520 g cm^{-3}. Single-crystal X-ray diffraction data were collected on a Picker FACS-1 automated diffractometer using a θ–2θ scan. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms were located, the final discrepancy indices being $R_F = 2.85\%$ and $R_{wF} = 3.20\%$ for the 1726 symmetry-independent reflections representing data complete to $2\theta = 45°$ (Mo Kα radiation). The crystallographic asymmetric unit contains one and one-third molecules of $[HB(C_3N_2H_3)_3]Cu(CO)$ and there are thus two crystallographically distinct types of molecule within the unit cell. One type of molecule has precise (i.e., crystallographically dictated) C_3 symmetry, while the other has no symmetry and is, in fact, somewhat distorted from the C_{3v} symmetry which the molecule could possess. The two independently determined copper(I)–carbonyl bond lengths are 1.755 (11) and 1.775 (5) Å [average 1.765 ± 0.014 Å]. Other bond distances fall into the following ranges: Cu–N = 2.039 (4)–2.059 (3) Å, C–O = 1.120 (6) and 1.120 (13) Å, N–N = 1.350 (5)–1.378 (5) Å, N–C = 1.331 (7)–1.361 (6) Å, C–C = 1.354 (8)–1.386 (8) Å, and N–B = 1.526 (6)–1.558 (6) Å. For the molecule lying on the crystallographic C_3 axis, bond angles around the copper(I) atom are C(1)–Cu(1)–N(11) = 124.4 (1)° and N(11)–Cu(1)–N(11′) = 91.3 (2)°. For the molecule lying in the general position, OC–Cu–N angles range from 119.4 (2) to 127.3 (2)° and N–Cu–N angles are 90.4 (1)–92.4 (2)°.

Introduction

Binary carbonyls, $M_x(CO)_y$, are known for each of the first-row transition elements from vanadium through nickel. There is, however, no stable (i.e., isolable under ambient conditions) binary carbonyl of copper, although evidence has accumulated for the existence of such species under extreme conditions, viz., as a short-lived intermediate following the passage of halogen-free carbon monoxide over heated copper,[3] as a surface species in chemisorption of carbon monoxide on metallic copper,[4,5] and as a product from the condensation of hot copper atoms onto a carbon monoxide matrix at 20°K.[6]

Carbonyl *complexes* of copper are confined to the copper(I) oxidation state. These species have been under investigation for some time.[7] Thus, in 1850 Leblanc[8a] showed that am-

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