complex $[IrHCl(HP(C_6H_5)_2)_4]^+$, owing to its limited solubility. However, the iridium–hydrogen stretching vibration falls at 2080 cm^{-1}, thus suggesting a trans arrangement of the hydride groups toward the phosphine.

Carbon monoxide readily reacted with the $[Ir(HPR_2)_4]^+$ complexes in methanol suspension, to produce the five-coordinate carbonyl derivatives $[Ir(CO)(HPR_2)_4]^+$ (HPR_2 = $HP(C_6H_5)_2$, $HP(C_6H_5)C_6H_{11}$) or $[Ir(CO)_2(HP(C_6H_{11})_2)_3]^+$. Carbonyl complexes of Ir(I) with secondary phosphines can also be obtained by reacting $[IrCl(CO)(P(C_6H_5)_3)_2]$ with an excess of secondary phosphine in methanol in the presence of $NaB(C_6H_5)_4$. By this route, the compounds $[Ir(CO)(HPR_2)_4]B(C_6H_5)_4$ (HPR_2 = $HP(C_2H_5)_2$, $HP(C_6H_5)_2$, and $HP(C_6H_5)C_6H_{11}$) and $[Ir(CO)(HP(C_6H_{11})_2)_3]B(C_6H_5)_4$ have been isolated. The latter complex, which can take up further carbon monoxide to yield $[Ir(CO)_2(HP(C_6H_{11})_2)_3]B(C_6H_5)_4$, easily gives oxidative addition reactions. I.e., the reaction with hydrogen yields *cis*-$[IrH_2(CO)(HP(C_6H_{11})_2)_3]^+$ (ν_{IrH} at 2140 and 2160 cm^{-1}), whose ^1H NMR spectra, in the high-field region, show a complex signal which arises from overlapping of a doublet of triplets (hydride trans to phosphine) on a quintet (hydride trans to carbonyl group). Additional splitting of the signals by H–H coupling (J_{H-H} = 2 Hz) is also observed.

Finally, the orange $[Ir(HPR_2)_4]^+$ complexes irreversibly take up oxygen in the solid state, giving cream-colored products, which probably are 1:1 adducts. However, the $Ir–O_2$ bands, in the 800–900-cm^{-1} region[13] could not be detected owing to the strong absorptions of the ligands and of the tetraphenylborate anion. Recrystallization of the crude products is accompanied by extensive decomposition and pure samples have not been obtained.

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Registry No. $[Rh(HPEt_2)_4]BPh_4$, 57109-24-7; $[Rh(HPEtPh)_4]ClO_4$, 57109-26-9; $[Rh(HPPh_2)_4]ClO_4$, 33990-36-2; $[Rh(HPPhCy)_4]ClO_4$, 57109-28-1; $[Rh(HPCy_2)_4]ClO_4$, 57109-29-2; *trans*-$[RhHCl(HPEt_2)_4]BPh_4$, 57109-31-6; *trans*-$[RhHCl(HPPhEt)_4]BPh_4$, 57109-33-8; $[RhHCl(HPPh_2)_4]ClO_4$, 57109-35-0; *cis*-$[RhHCl(HPPhCy)_4]ClO_4$, 57109-37-2; *cis*-$[RhHCl(HPPhCy)_4]BPh_4$, 57109-38-3; *trans*-$[RhHCl(HPCy_2)_4]ClO_4$, 57109-40-7; $[RhCl(HPCy_2)_3]$, 55017-05-5; $[Rh(CO)(HPCy_2)_3]ClO_4$, 57109-42-9; $[IrH(HPEt_2)_5](ClO_4)_2$, 57109-44-1; $[IrH(HPEt_2)_5](BPh_4)_2$, 57109-45-2; $[Ir(HPPh_2)_4]BPh_4$, 57109-47-4; $[Ir(HPPhCy)_4]BPh_4$, 57109-49-6; $[Ir(HPCy_2)_4]BPh_4$, 57109-51-0; $[Ir(CO)(HPEt_2)_4]BPh_4$, 57109-53-2; $[Ir(CO)(HPPh_2)_4]BPh_4$, 33990-20-4; $[Ir(CO)(HPPhCy)_4]BPh_4$, 57109-55-4; $[Ir(CO)(HPCy_2)_3]BPh_4$, 57109-57-6; $[Ir(CO)_2(HPCy_2)_3]BPh_4$, 57109-59-8; *cis*-$[IrH_2(HPPh_2)_4]BPh_4$, 57109-61-2; *cis*-$[IrH_2(HPPhCy)_4]BPh_4$, 57109-63-4; *cis*-$[IrH_2(HPCy_2)_4]BPh_4$, 57109-65-6; $[IrHCl(HPPh_2)_4]BPh_4$, 57109-67-8; *trans*-$[IrHCl(HPPhCy)_4]BPh_4$, 57109-69-0; *trans*-$[IrHCl(HPCy_2)_4]BPh_4$, 57109-71-4; *cis*-$[IrH_2(CO)(HPCy_2)_3]BPh_4$, 57109-73-6; $[RhCl(C_8H_{12})]_2$, 12092-47-6; $[IrCl(C_8H_{14})_2]_2$, 12246-51-4; *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I), 15318-31-7; HCl, 7647-01-0.

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Molecular Structure of *trans*-Methyliodo[difluoro[3,3'-(trimethylenedinitrilo)bis(2-pentanone oximato)]borate]rhodium(III)

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The structure of *trans*-methyliodo[difluoro[3,3'-(trimethylenedinitrilo)bis(2-pentanone oximato)]borate]rhodium(III), $Rh(CH_3)I[C_2(DO)(DOBF_2)]$, has been determined from three-dimensional x-ray diffraction data collected by counter methods using θ-2θ scans. The octahedrally coordinated Rh ion lies in the plane of the four N atoms of the macrocyclic ligand. The methyl and iodide occupy axial positions with bond distances Rh–C = 2.090 (4) Å and Rh–I = 2.813 (0) Å. The overall ligand conformation resembles the "chair" conformation of cyclohexane with the BF_2 bridge bent toward the axial methyl and the propylene bridge toward the iodide. The shortest axial methyl C–F distance of 3.11 Å is close to the sum of the van der Waals radii. The ^1H NMR spectrum in CD_2Cl_2 exhibits spin coupling of the axial methyl protons with ^{19}F in the BF_2 bridge (J_{H-F} = 2.3 Hz), consistent with a weak CH···F interaction. The dark orange crystals of $Rh(CH_3)I[C_2(DO)(DOBF_2)]$ conform to the space group $P2_1/n$ with a = 9.424 (4) Å, b = 17.36 (1) Å, c = 12.40 (1) Å, and β = 94.18 (5)°; Z = 4; $\rho_{calcd} = \rho_{obsd}$ = 1.84 g/cm^3. The structure was refined anisotropically by full-matrix least squares using 2977 reflections with $|F_o|^2 > 3\sigma(|F_o|^2)$ to give R_1 = 0.031 and R_2 = 0.038.

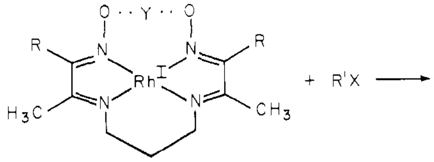
Introduction

The coordinatively unsaturated, square-planar complex of rhodium(I) with tetradentate 3,3'-(trimethylenedinitrilo)bis(2-butanone oximate),[2] $[(DOH)_2pn]$, **1a**, is one of the most reactive neutral d^8 complexes toward oxidative addition[3] reactions yet isolated.[4] Primary and secondary alkyl halides readily form rhodium(III) adducts in high yield (eq 1). Steric constraints imposed by the rigid macrocycle are thought to enforce trans addition. Recent kinetic studies have revealed a marked neighboring-group effect for α,ω-dihaloalkyls during oxidative addition reactions with rhodium(I) complexes of 3,3'-(trimethylenedinitrilo)bis(2-pentanone oximate), $[C_2(DOH)_2pn]$, and its BF_2-bridged derivative[5] **1b**. Since 1,4-dibromocyclohexane fails to afford any product other than

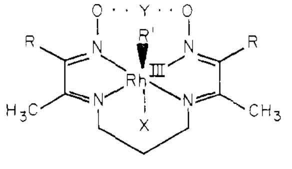
Table I. Summary of Crystal Data

Molecular formula	$Rh(CH_3)I(C_{13}H_{22}N_4O_2BF_2)$
Mol wt	560.00
Space group	$P2_1/n$
Cell constants[a]	
a	9.424 (4) Å
b	17.36 (1) Å
c	12.40 (1) Å
β	94.18 (5)°
Cell volume	2023 (4) Å^3
Formula units/unit cell	4
Calcd density	1.84 g/cm^3
Obsd density	1.84 g/cm^3
Crystal dimensions	0.015 × 0.015 × 0.040 cm
Linear absorption coeff, μ	23.99 cm^{-1}

[a] Ambient temperature of 21°, Mo Kα radiation, λ 0.70926 Å.



1a, R = CH_3, Y = H
1b, R = CH_3CH_2, Y = H, BF_2



(1)

a simple monorhodium adduct, a cyclic intermediate has been proposed.[5] This would require cis coordination sites and thus distortion of the macrocycle from planarity. It has been found that activated olefins and acetylenes (TCNE, dimethyl fumarate, and dimethyl acetylenedicarboxylate) form stable 1:1 adducts with $Rh[C_2(DO)(DOBF_2)]$ in which the ligand is nonplanar, as evidenced by ^1H NMR spectra.[4] Structural analysis of the simple methyl iodide adduct of $Rh[C_2(DO)(DOBF_2)]$, **2**, was carried out to verify the expected coordination geometry and also to serve as a point of reference for future x-ray studies.

Experimental Section

$Rh(CH_3)I[C_2(DO)(DOBF_2)]$ was prepared as described previously.[4,6] Crystals suitable for x-ray analysis were prepared by slow vapor diffusion of diethyl ether into a saturated dichloromethane solution of the complex at room temperature.

A dark orange parallelepiped-shaped crystal with approximate dimensions 0.15 × 0.15 × 0.40 mm was mounted on a glass fiber using epoxy cement such that the longest crystal dimension was approximately parallel to the fiber axis.

Unit cell parameters and the orientation matrix were determined on a Syntex $P2_1$ four-circle diffractometer equipped with a single-crystal graphite monochromator (Bragg 2θ angle 12.2°) using Mo Kα radiation at a takeoff angle of 3.0°. Fifteen reflections whose 2θ values ranged from 4.89 to 15.79° were machine centered and used in a least-squares refinement of the lattice parameters and orientation matrix. Unit cell parameters and other pertinent crystal data are summarized in Table I. The observed density (by flotation in 1,-2-dibromoethane–heptane) and the calculated density were both 1.84 g/cm^3 using four molecules per unit cell. Axial photographs indicated that the crystal belonged to the monoclinic system. ω scans of several low 2θ angle reflections gave average peak widths at half-height of less than 0.30°, indicating mosaicity low enough for data collection.

Intensity data were collected using θ–2θ scans with x-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable-scan rate from 2.02 to 29.30° min^{-1} was used for the intensity measurements. A scan width of 1.70° sufficed to collect all the peak intensity. Stationary-background counts were measured at the beginning and end of each scan with a total background to scan time ratio of 0.25. No significant fluctuations were observed in the intensities of three standard reflections (3,0,−1; 0,−2,1; 1,4,1) monitored every 50 reflections.

A full form of data ($h,k,\pm l$) was measured out to $2\theta_{max} = 50°$. A total of 3946 reflections were collected. The data processing was carried out by our program ENXDR.[7] The parameter p, introduced to avoid overweighting the strong reflections, was set to 0.03. The corrected intensities were converted to values of F^2 by application of Lorentz and polarization corrections. An absorption correction was not applied. The linear absorption coefficient was 23.99 cm^{-1} and the values of μt ranged from 0.360 to 0.960. There were 2977 reflections with $|F_o|^2 > 3\sigma(|F_o|^2)$ which were used in the final refinement.

Careful examination of zero- and upper-level computer-generated precession photographs, as well as the intensities themselves, clearly revealed systematic absences for the class of reflections $h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$). The space group $P2_1/n$ (an alternate setting of $P2_1/c$, C_{2h}^5) is the only group consistent with these conditions.

The structure was solved by heavy-atom techniques. Full-matrix least-squares refinements on F were used in which the function minimized was $\sum w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors.[7] The weighting factor, w is given by $w = 4F_o^2/\sigma^2(F_o^2)$ where (F_o^2) is calculated by

$$I = N_{\mathbf{T}} - 4(N_{\mathbf{B1}} + N_{\mathbf{B2}})$$

$$\sigma(F_0^{\,2}) = [N_{\mathbf{T}} + J^2(N_{\mathbf{B1}} + N_{\mathbf{B2}}) + (pI)^2]^{1/2}/L$$

where N_T, N_{B1}, and N_{B2} are the total peak and two background counts, J is the ratio of peak scan time to background scan time, and L is the Lorentz–polarization factor. The atomic scattering factors for neutral Rh, I, C, N, O, F, B, and H were taken from the values tabulated in ref 8.

Correction for anomalous dispersion effects of the nonhydrogen atoms using both $\Delta f'$ and $\Delta f''$ were included in the calculations of the F's.

The coordinates for the rhodium and iodine atoms were obtained from a three-dimensional Patterson map. These atoms occupy general positions in the unit cell. With only the Rh and I atoms in the structure factor calculation, after three cycles of refinement, the unweighted R factor, R_1, given by $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, was 0.255. A difference Fourier map was calculated from which all the remaining nonhydrogen atoms were located. Using anisotropic temperature factors for the Rh and I and isotropic temperature factors for the other nonhydrogen atoms, the refinement (111 variables) converged to an R_1 of 0.061. The weighted R factor, R_2, given by $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, was 0.073. Refinement employing all nonhydrogen atoms with anisotropic temperature factors (226 variables) converged to $R_1 = 0.034$. Hydrogen atom positions were calculated by the program HYGEN using a C–H bond distance of 1.1 Å for methyl hydrogens and 1.07 Å for methylene hydrogens. Isotropic temperature factors for the hydrogens were set at 3.0 Å.[2] Inclusion of the fixed hydrogen atoms in the final structure factor calculations lowered R_1 to 0.031 and R_2 to 0.038. In the final cycle the largest shift per standard deviation was 0.05. The final difference Fourier map showed no peaks unattributable to residual density around the rhodium and iodine atoms. Observed and calculated structure factors for the data set are available.[9]

Atomic positional parameters and anisotropic thermal parameters are listed in Table II. Table III gives the root-mean-square (rms) amplitudes of vibration along the principal axes of the thermal ellipsoids for all nonhydrogen atoms.

Discussion

The crystal structure consists of discrete $Rh(CH_3)I[C_2(DO)(DOBF_2)]$ molecules with the molecular configuration shown in Figure 1. No unusual crystal-packing effects were observed. Bond distances and angles are listed in Table IV.

The octahedrally coordinated rhodium lies in the plane of the four N atoms of the macrocycle (Table V) as was also observed in $Rh[(DO)(DOH)]$[10] and $[Co(CH_3)(H_2O\{(DO)(DOH)\}]ClO_4$.[11] The Rh–N bond distances and angles are almost identical with those in $Rh[(DO)(DOH)]$ and are consistent with those in rhodium(III)–bis(dimethylglyoxime) complexes (Table VI). The Rh^{III}–N bond distances average 0.1 Å longer than the corresponding Co^{III}–N distances. The

Table II. Atomic Positional and Thermal Parameters and Estimated Standard Deviations[a]

Atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
I	0.16548 (4)	0.24388 (2)	0.30228 (3)	0.01281 (5)	0.00300 (1)	0.00526 (2)	−0.00137 (4)	−0.00120 (6)	−0.00121 (3)
Rh	0.06805 (4)	0.16389 (2)	0.11396 (3)	0.00681 (4)	0.00170 (1)	0.00457 (2)	0.00042 (4)	0.00149 (5)	−0.00050 (3)
F1	−0.3164 (3)	0.0849 (2)	0.2776 (3)	0.0126 (4)	0.0032 (1)	0.0108 (3)	−0.0020 (4)	0.0107 (5)	−0.0007 (3)
F2	−0.2570 (3)	0.0644 (2)	0.1049 (3)	0.0112 (4)	0.0036 (1)	0.0091 (3)	−0.0016 (4)	0.0003 (6)	−0.0030 (3)
O1	−0.0829 (4)	0.0605 (2)	0.2520 (3)	0.0094 (4)	0.0025 (1)	0.0071 (3)	−0.0003 (4)	0.0041 (6)	0.0008 (3)
O2	−0.2154 (4)	0.1845 (2)	0.1911 (3)	0.0079 (4)	0.0023 (1)	0.0082 (3)	0.0001 (4)	0.0065 (5)	−0.0003 (3)
N1	0.0370 (4)	0.0708 (2)	0.1995 (3)	0.0088 (5)	0.0019 (1)	0.0059 (3)	−0.0004 (5)	0.0014 (6)	−0.0010 (3)
N2	0.2549 (4)	0.1097 (2)	0.1036 (3)	0.0075 (5)	0.0026 (1)	0.0062 (3)	0.0015 (5)	0.0016 (6)	−0.0006 (4)
N3	0.0909 (4)	0.2586 (2)	0.0251 (3)	0.0090 (5)	0.0023 (1)	0.0049 (3)	0.0001 (5)	0.0006 (6)	−0.0002 (3)
N4	−0.1172 (4)	0.2130 (2)	0.1252 (3)	0.0071 (4)	0.0020 (1)	0.0053 (3)	−0.0002 (4)	0.0017 (6)	−0.0005 (3)
C1	−0.0048 (6)	0.1097 (3)	−0.0300 (4)	0.0127 (7)	0.0023 (2)	0.0050 (3)	0.0004 (6)	0.0011 (9)	−0.0016 (4)
C2	0.1670 (11)	−0.0299 (4)	0.4021 (6)	0.0391 (18)	0.0044 (3)	0.0080 (5)	−0.0048 (13)	−0.0102 (17)	0.0031 (7)
C3	0.1310 (6)	−0.0472 (3)	0.2831 (5)	0.0131 (8)	0.0019 (2)	0.0102 (5)	−0.0000 (6)	−0.0034 (11)	0.0009 (5)
C4	0.1409 (5)	0.0213 (3)	0.2134 (4)	0.0099 (6)	0.0017 (1)	0.0058 (3)	0.0012 (5)	−0.0023 (8)	−0.0019 (4)
C5	0.2653 (5)	0.0436 (3)	0.1550 (4)	0.0077 (6)	0.0026 (2)	0.0064 (3)	0.0018 (6)	−0.0005 (8)	−0.0022 (4)
C6	0.3926 (6)	−0.0089 (3)	0.1543 (5)	0.0117 (7)	0.0032 (2)	0.0112 (5)	0.0052 (7)	−0.0016 (11)	−0.0011 (6)
C7	0.3614 (6)	0.1426 (3)	0.0368 (5)	0.0093 (6)	0.0038 (2)	0.0075 (4)	0.0020 (7)	0.0054 (9)	0.0004 (5)
C8	0.3523 (6)	0.2313 (4)	0.0287 (5)	0.0092 (6)	0.0042 (2)	0.0092 (5)	−0.0020 (7)	0.0055 (9)	0.0019 (6)
C9	0.2218 (6)	0.2671 (3)	−0.0343 (4)	0.0114 (7)	0.0035 (2)	0.0067 (4)	−0.0002 (7)	0.0057 (9)	0.0016 (5)
C10	−0.0255 (7)	0.3781 (3)	−0.0427 (5)	0.0146 (8)	0.0029 (2)	0.0092 (5)	0.0005 (7)	0.0030 (11)	0.0035 (5)
C11	−0.0155 (6)	0.3048 (3)	0.0194 (4)	0.0102 (6)	0.0021 (2)	0.0052 (3)	−0.0004 (6)	0.0009 (8)	0.0002 (4)
C12	−0.1382 (5)	0.2806 (3)	0.0817 (4)	0.0085 (6)	0.0023 (2)	0.0054 (3)	0.0000 (6)	−0.0015 (8)	−0.0014 (4)
C13	−0.2600 (6)	0.3320 (3)	0.1039 (5)	0.0089 (6)	0.0023 (2)	0.0092 (4)	0.0023 (6)	0.0007 (9)	0.0000 (5)
C14	−0.2173 (8)	0.3885 (4)	0.1943 (6)	0.0166 (9)	0.0039 (2)	0.0133 (6)	0.0052 (8)	0.0040 (13)	−0.0060 (6)
B	−0.2175 (7)	0.0979 (3)	0.2023 (5)	0.0089 (7)	0.0023 (2)	0.0080 (5)	−0.0017 (6)	0.005 (1)	−0.0009 (5)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H1	−0.0105 (0)	0.0478 (0)	−0.0181 (0)	3.0000 (0)	H14	0.4451 (0)	0.2526 (0)	−0.0047 (0)	3.0000 (0)
H2	−0.1122 (0)	0.1322 (0)	−0.0562 (0)	3.0000 (0)	H15	0.3509 (0)	0.2533 (0)	0.1116 (0)	3.0000 (0)
H3	0.0677 (0)	0.1231 (0)	−0.0935 (0)	3.0000 (0)	H16	0.2072 (0)	0.2381 (0)	−0.1108 (0)	3.0000 (0)
H4	0.1597 (0)	−0.0799 (0)	0.4547 (0)	3.0000 (0)	H17	0.2411 (0)	0.3270 (0)	−0.0479 (0)	3.0000 (0)
H5	0.2769 (0)	−0.0053 (0)	0.4147 (0)	3.0000 (0)	H18	0.0742 (0)	0.3866 (0)	−0.0841 (0)	3.0000 (0)
H6	0.0930 (0)	0.0159 (0)	0.4304 (0)	3.0000 (0)	H19	−0.1155 (0)	0.3757 (0)	−0.1034 (0)	3.0000 (0)
H7	0.0243 (0)	−0.0709 (0)	0.2742 (0)	3.0000 (0)	H20	−0.0382 (0)	0.4264 (0)	0.0128 (0)	3.0000 (0)
H8	0.2032 (0)	−0.0914 (0)	0.2588 (0)	3.0000 (0)	H21	−0.3485 (0)	0.2969 (0)	0.1254 (0)	3.0000 (0)
H9	0.4761 (0)	0.0158 (0)	0.1058 (0)	3.0000 (0)	H22	−0.2935 (0)	0.3628 (0)	0.0304 (0)	3.0000 (0)
H10	0.4397 (0)	−0.0190 (0)	0.2374 (0)	3.0000 (0)	H23	−0.3071 (0)	0.4264 (0)	0.2104 (0)	3.0000 (0)
H11	0.3613 (0)	−0.0658 (0)	0.1183 (0)	3.0000 (0)	H24	−0.1838 (0)	0.3565 (0)	0.2691 (0)	3.0000 (0)
H12	0.4662 (0)	0.1263 (0)	0.0718 (0)	3.0000 (0)	H25	−0.1273 (0)	0.4243 (0)	0.1715 (0)	3.0000 (0)
H13	0.3477 (0)	0.1184 (0)	−0.0427 (0)	3.0000 (0)					

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

Table III. Root-Mean-Square Amplitudes of Vibration of All Nonhydrogen Atoms along the Principal Axes (Å × 10^3)

Atom	Axis 1	Axis 2	Axis 3	Atom	Axis 1	Axis 2	Axis 3
Rh	156	191	176	C12	226	191	168
I	183	247	224	C13	268	217	166
C1	166	239	214	C14	172	350	291
C2	441	262	214	N1	164	218	198
C3	298	227	168	N2	170	222	207
C4	243	190	145	N3	202	195	188
C5	247	189	166	N4	205	176	172
C6	171	307	258	O1	243	202	186
C7	181	260	237	O2	263	190	165
C8	178	282	253	F1	314	224	189
C9	186	257	230	F2	285	235	200
C10	187	287	253	B	257	198	173
C11	178	215	201				

best least-squares planes passing through the mirror-related halves of the chelate (Table V) intersect with a 2.64° dihedral angle compared to 2.46 and 2.7° for the Rh^{I}– and Co^{III}–[(DO)(DOH)] complexes, respectively.

The Rh–C(1) bond distance is comparable to other Rh^{III}–alkyl bond distances (Table VII). The Rh–I bond is slightly longer than most Rh^{III}–I bonds (Table VII), reflecting the strong trans influence of the methyl group.[12] The methyl group is slightly inclined away from the BF$_2$ bridging group.

The distance between O(1) and O(2) (2.575 Å) is identical with that found in the Rh[(DO)(DOH)] complex with the simple H bridge (2.56 Å)[10] but is almost 0.2 Å longer than in the Co^{III}[(DO)(DOH)] complex (2.39 Å).[11] Also, O(1) and O(2) lie slightly below the ligand plane (Table V).

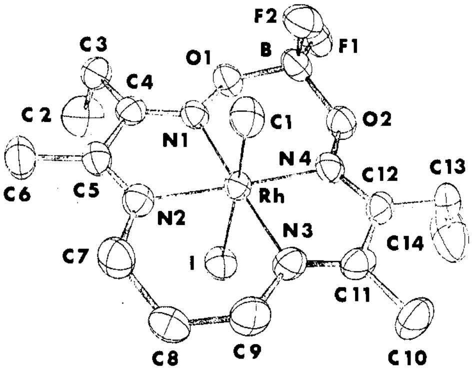


Figure 1. ORTEP thermal ellipsoid plot (50% probability) and atomic numbering scheme. The hydrogen atoms have been omitted for clarity.

The orientation of the BF$_2$ bridge is particularly interesting. The B atom lies 0.500 (6) Å above the plane of the macrocycle (Table V) and is inclined toward C(1) with F(2) directed toward C(1). The C(1)–F(2) distance of 3.106 Å is slightly longer than the sum of the van der Waals radii (3.0 Å).[13] Although the distances from F(2) to the closest calculated C(1) hydrogen positions (2.88, 2.76 Å) are only about 0.2 Å longer than the sum of van der Waals radii, the actual hydrogen atom positions were not determined and, thus, the existence of a weak hydrogen bond involving C(1) and F(2)[14,15] cannot be concluded with certainty.

Table IV. Bond Distances and Bond Angles with Corresponding Estimated Standard Deviations

	Distances, Å		
Rh–I	2.813 (0)	C7–C8	1.545 (7)
Rh–C1	2.090 (4)	C8–C9	1.538 (7)
Rh–N1	1.966 (3)	N3–C9	1.489 (6)
Rh–N2	2.009 (3)	N3–C11	1.282 (5)
Rh–N3	1.999 (3)	C11–C10	1.487 (6)
Rh–N4	1.957 (3)	C11–C12	1.496 (6)
N1–O1	1.357 (4)	C12–C13	1.495 (6)
N1–C4	1.305 (5)	C13–C14	1.522 (7)
C3–C4	1.477 (6)	N4–C12	1.301 (5)
C3–C2	1.520 (7)	N4–O2	1.371 (4)
C4–C5	1.474 (6)	O2–B	1.511 (6)
C5–C6	1.507 (6)	F1–B	1.384 (6)
N2–C5	1.312 (5)	F2–B	1.368 (6)
N2–C7	1.463 (6)		
	Angles, Deg		
I–Rh–C1	177.2 (1)	C7–C8–C9	118.3 (4)
N1–Rh–N2	79.3 (1)	C8–C9–N3	111.6 (4)
N1–Rh–N4	98.7 (1)	C9–N3–C11	125.7 (3)
N2–Rh–N3	102.7 (1)	N3–C11–C12	115.3 (4)
N3–Rh–N4	79.3 (1)	C11–C12–O2	111.6 (4)
O1–B–O2	116.6 (4)	C12–N4–O2	118.9 (3)
O1–B–F1	103.9 (4)	C2–C3–C4	112.9 (4)
O1–B–F2	110.1 (4)	C3–C4–C5	125.8 (4)
O2–B–F1	103.8 (4)	C3–C4–N1	122.0 (4)
O2–B–F2	110.3 (4)	C6–C5–C4	120.4 (4)
F1–B–F2	111.9 (4)	C6–C5–N2	123.9 (4)
O1–N1–C4	119.5 (3)	C10–C11–N3	125.7 (4)
N1–C4–C5	112.2 (4)	C10–C11–C12	119.0 (4)
C4–C5–N2	115.7 (3)	C14–C13–C12	110.8 (4)
C5–N2–C7	125.9 (3)	C13–C12–C11	124.1 (4)
N2–C7–C8	112.9 (4)	C13–C12–N4	123.8 (4)

Table V. Selected Least-Squares Planes[7]

(i) Atoms in Plane: N1, N2, N3, N4, Rh

Equation: $-0.3058X - 0.4809Y - 0.8217Z = -2.6903$

	Distances from Plane, Å		
N1	0.020 (4)	O1	−0.067 (3)
N2	0.016 (4)	O2	−0.119 (3)
N3	0.021 (4)	C7	0.094 (6)
N4	0.013 (4)	C8	−0.539 (6)
Rh	−0.001 (4)	C9	0.161 (6)
B	0.500 (6)	C1	2.085 (5)

(ii) Atoms in Plane: N1, N2, C4, C5

Equation: $-0.3074X - 0.4857Y - 0.8183Z = -2.6754$

	Distances from Plane, Å		
N1	0.008 (4)	C4	−0.013 (5)
N2	−0.008 (4)	C5	0.013 (6)

(iii) Atoms in Plane: N3, N4, C11, C12

Equation: $0.3362X - 0.4508Y - 0.8269Z = -2.5487$

	Distances from Plane, Å		
N3	−0.012 (4)	C11	0.020 (5)
N4	0.012 (4)	C12	−0.020 (5)

(iv) Atoms in Plane: O1, O2, B

Equation: $0.4078X - 0.0918Y - 0.9085Z = -3.3396$

	Distances from Plane, Å		
F1	−1.232 (3)	F2	1.033 (3)

	Dihedral Angles between Planes, Deg		
ii–iii	2.64	i–iv	48.28

The 100-MHz ^{1}H NMR spectrum of $Rh(CH_3)I[C_2(DO)(DOBF_2)]$ in CD_2Cl_2 exhibited an unexpected splitting of the metal-bonded methyl group resonance.[16] A doublet of doublets ($J = 2.3$ Hz) was observed instead of a single doublet due to $^{103}Rh(I = {}^1/_2)$ coupling. Since the corresponding resonance is a doublet ($J_{Rh-H} = 2.5$ Hz) in the spectrum of $Rh(CH_3)I[(DO)(DOH)]$, it was suspected that the additional splitting arose from spin coupling with $^{19}F(I = {}^1/_2)$ in the BF_2 bridge. This coupling was confirmed when irradiation at the resonant frequencies of the BF_2 bridge F atoms gave a well-resolved doublet ($J_{Rh-H} = 2.5$ Hz). Examples of long-range $^{19}F-^1H$ coupling have been reported for organic[17] and organometallic[18] compounds. This coupling may occur either through bonds or through space. Since the shortest through-bond route traverses *six* bonds, a through-space coupling is more tenable, especially if the coordination geometry allows a close approach of the coupled nuclei.[19] Although the conformation in solution is not known, a weak CH···F interaction is indicated and is consistent with the solid-state structure.

The conformation of the propylene bridge (C(7), C(8), C(9)) is that in which C(8) lies below the macrocycle plane. This produces an overall ligand conformation which resembles the "chair" conformer of cyclohexane. The BF_2 bridge is bent away from the large I^- ion and the propylene bridge is bent downward to avoid crowding around C(1).

Table VI. Metal–Macrocycle Coordination

Complex	Distances, Å		Angles, Å		
	M–N1	M–N2	N1–M–N4	N2–M–N3	N1–M–N2
$Rh(CH_3)I[C_2(DOBF_2)]$[a]	1.96	2.00	98.7	102.7	79.3
$Rh(DO)(DOH)$[b]	1.95	1.99	100.2	101.8	79.0
$RhCl(PPh_3)(dmg)_2$[c]	1.99		100.5		79.0
$H[RhCl_2(dmg)_2]$[d]	2.01		102.0		78.0
$[Co(CH_3)(H_2O)\{(DO)(DOH)\}]ClO_4$[e]	1.87	1.93	98.4	98.4	81.5
$Co(CH_3)(H_2O)(dmg)_2$[f,g]	1.89 1.88		98.6 98.2		81.3 81.7

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Table VII. Rhodium(III)–Alkyl and –Iodide Bond Distances (Å)

Complex	Rh–alkyl	Rh–I	Ref
$RhI(CH_3)[C_2(DO)(DOBF_2)]$	2.09	2.81[a]	*b*
$RhI(\pi\text{-}C_5H_5)(C_2F_5)(CO)$	2.08	2.65	*c*
$RhI_2(CH_3)(PPh_3)_2\cdot C_6H_6$	2.08	2.64	*d*
$[RhCl_2(C_8H_{15}O_2)(CH_3C_5H_4N)_2]_2$	2.07		*e*
$[Rh(C_2H_5)(NH_3)_5]Br$	2.05		*f*
$Rh_2I_2(S(CH_3)_2)_3(CH_3)_4$	2.26	*a, g*	*h*
$RhI_3(CO)(CPh(NCH_3)CPhNCH_3)$	1.97	2.67, 2.77[a]	*i*
$[RhI_2(C_2H_4N)_4]I$		2.68	*j*
$[(n\text{-}C_3H_7)_4N][RhI_4(CO)_2]$		2.69[k]	*l*

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Registry No. $Rh(CH_3)I[C_2(DO)(DOBF_2)]$, 57255-98-8.

Supplementary Material Available: Listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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Studies of Boranes. XLV.[1] Crystal and Molecular Structure, Improved Synthesis, and Reactions of Tridecaborane(19)

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The crystal and molecular structure of $B_{13}H_{19}$ has been determined by a single-crystal X-ray diffraction study. The compound crystallizes in space group $P2_1/c$ with $a = 9.217$ (2) Å, $b = 6.498$ (3) Å, $c = 19.719$ (5) Å, and $\beta = 97.69$ (1)°. The calculated density for $Z = 4$ is 0.91 g/cm³. The structure was solved by direct methods and refined to residuals $R_1 = 0.113$ and $R_2 = 0.055$. The structure can be described as an n-B_9H_{15} cage sharing two borons with a B_6H_{10} cage; however, the B_9 skeleton lacks the m symmetry present in n-B_9H_{15}. An improved synthesis of $B_{13}H_{19}$ has been obtained by the following reaction scheme: $KB_6H_8Br + {}^1/_2B_2H_6 \rightarrow KB_7H_{11}Br$; $KB_7H_{11}Br + B_6H_{10} \rightarrow B_{13}H_{19} + H_2 + KBr$. Reaction of $B_{13}H_{19}$ with potassium hydride yielded the relatively stable $KB_{13}H_{18}$, which regenerated $B_{13}H_{19}$ upon acidification. The ^{11}B NMR spectra of normal and isotopically labeled (^{10}B and ^2D) $B_{13}H_{19}$ and $KB_{13}H_{18}$ are discussed in relation to their structures.

Introduction

Tridecaborane(19) was first prepared in our laboratory in trace quantities from the pyrolysis of hexaborane(10) and subsequently was obtained in low yield by the generation of $[B_7H_{11}]$ in the presence of hexaborane(10).[2] Structural studies were undertaken and a preliminary report of the X-ray crystal structure has appeared,[3] but reaction studies of tridecaborane(19) were hindered by the relatively small amounts of this material available.

In this work the complete analysis of the crystal and molecular structure of $B_{13}H_{19}$ is presented. We also wish to report an improved synthesis of $B_{13}H_{19}$ which involves the generation of the $[B_7H_{11}]$ intermediate by KBr elimination from $KB_7H_{11}Br$ in the presence of hexaborane(10). The deprotonation of $B_{13}H_{19}$ to yield $KB_{13}H_{18}$ is described, along with attempts to generate a B_{14} species by borane addition to this anion. Studies involving ^{10}B and ^2D isotopic substitution are also presented.

Experimental Section

Crystallography—Crystal Data. A well-formed crystal of approximate dimensions 0.3 mm × 0.3 mm × 0.4 mm was utilized in the crystallographic study.[4] Preliminary precession photographs and a diffractometer search of the reciprocal lattice indicated $2/m$ Laue symmetry with conditions for nonextinction of $l = 2n$ for $h0l$ and $k = 2n$ for $0k0$, uniquely determining the space group to be $P2_1/c$ (No. 14, C_{2h}^5). A least-squares fit of angular data from 16 reflections centered in $\pm 2\theta$ yielded cell parameters of $a = 9.217$ (2) Å, $b = 6.498$ (3) Å, $c = 19.719$ (5) Å, and $\beta = 97.69$ (1)° (at ca. −130°). The calculated density of $d_{\text{calcd}} = 0.91$ g/cm³ for $Z = 4$ is reasonable for compounds of this type.

Crystallography—Intensity Data Collection. Data were collected on a Picker FACS-1 diffractometer utilizing Mo Kα radiation (λ 0.71069 Å) monochromatized by a highly oriented graphite monochromator (002 plane, $2\theta_m = 12.06°$). Other diffractometer constants and data reduction formula are given elsewhere for the continuous θ–2θ scan technique used.[5]

Examination of ω and 2θ scans indicated a crystal of suitable mosaic character with no abnormalities. Three reflections chosen as standards were monitored after every 50 measurements and indicated no systematic changes in intensity. A total of 4023 reflections, including redundancies, were collected in the region $0° \leq 2\theta \leq 50°$ and reduced to 1763 unique intensities. The 729 reflections with $I \geq 2.33\sigma(I)$ were utilized in the solution and preliminary refinement of the structure, and all data were utilized in final refinement. No absorption corrections were made ($\mu = 0.36$ cm^{-1}). Preliminary scale and thermal parameters were determined by Wilson's method.[6]

Crystallography—Solution and Refinement of the Structure. Direct methods were used to assign phases to the 213 largest normalized structure factors, $Ehkl$, and an E map phased on these values located all 13 boron atoms in the structure. Isotropic least-squares refinement followed by a difference Fourier synthesis was used to locate all hydrogen atoms.[7] Full-matrix least squares were utilized to refine all positional parameters, anisotropic boron thermal parameters, isotropic hydrogen parameters, and an overall scale factor and isotropic extinction parameter. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 4I/(\sigma(I))^2$. A total of 1581 reflections were nonzero and thus had nonzero weight, giving a ratio of 8:1 for observations to parameters in the refinement. For the final cycle, the largest Δ/σ was 0.05, the goodness of fit was 1.16, and the extinction parameter was 1.8 (6) × 10^{-6}. The maximum extinction was 4.7% for the 004 reflection. The final residuals were $R_1 = 0.113$ and $R_2 = 0.055$ where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. The variance–covariance matrix was utilized to determine errors in bond distances and angles.

A final list of observed and calculated structure factors is available (see paragraph at end of paper regarding supplementary data).

Apparatus and Materials. Standard high-vacuum techniques were used throughout this investigation. The 70.6-MHz ^{11}B NMR spectra were recorded on a Varian Associates HR-220 spectrometer equipped with a "home-built" pulse apparatus. Mass spectra were obtained with a Varian Associates CH-7 mass spectrometer. Only thoroughly dried reagent grade solvents were used in this study. Normal B_2H_6, $^{10}B_2H_6$ (92% ^{10}B), and B_2D_6 (>95% ^2D) were obtained from laboratory supplies. Hexaborane(10) was prepared by literature procedure.[8] Dimethyl ether, trimethylamine, and hydrogen chloride were