10^{-5} M in the presence of 1 M norbornane, good first-order disappearance of oxidant was observed with $\mathbf{2}^+Cl^-$, and hemin loss was slight although the spectrum changed somewhat.

These observations show that $\mathbf{2}^+Cl^-$ (Fe^{III}88TPP) is an extraordinarily stable catalyst for hydroxylation or epoxidation. The simplicity and high yield of the synthesis of $\mathbf{2}^+Cl^-$ are also an advantage.[15] Thus substitution of bulky, electronegative groups on both the ortho and pyrrole positions lead to very effective catalysts. Conversion of the octabromoporphyrin to octacyanoporphyrin and the preparation of perchlorinated tetraphenylporphyrins are underway to further test these ideas.[16]

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE 84-20612) for support of this research.

Registry No. **1**-Zn, 100506-72-7; **1**-Fe(Cl), 91042-27-2; **2**, 107035-95-0; **2**-Zn, 107053-19-0; **2**-Fe(Cl), 107053-17-8; **2**-Fe(OH), 107053-18-9; norbornane, 279-23-2; pentafluoroiodosylbenzene, 14353-90-3; tetraphenylhemin chloride, 16456-81-8; cholestane, 481-21-0; tetrakis-(pentafluorophenyl)hemin chloride, 36965-71-6; 4,4-dimethyl-1-pentene, 762-62-9.

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(15) Improved syntheses of **1P** yield will be reported elsewhere.

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Structure and Characterization of $(C_5H_5)_2Zr(H)BH_3CH_3$

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Most well-characterized zirconium hydrides are obtained as derivatives of dicyclopentadienylzirconium, the first of which was prepared by treating $Cp_2Zr(BH_4)_2$ with trimethylamine (Cp = η^5-C_5H_5).[1] Other zirconium hydrides have also been synthesized by reacting $LiAlH_4$, $LiAl(O\text{-}t\text{-}C_4H_9)_3H$, $LiBH_4$, and $CH(CH_3)_2MgCl$ with various starting materials.[2] Most of these hydrides are polymeric and hence insoluble in organic solvents, thereby limiting studies of their physical and chemical properties. Consequently, very little structural information is available. The monomeric hydride $Cp_2Zr(H)BH_3CH_3$ has been isolated and structurally characterized during our unsuccessful attempt to synthesize $Cp_2Zr(BH_3CH_3)_2$.

Experimental Section

All manipulations were conducted under an inert atmosphere on a Schlenk line or in an inert-atmosphere glovebox. Solvents were dried and purged according to standard procedures. The ^1H (89.5 MHz) and ^{11}B (28.7 MHz) NMR spectra were recorded on a JEOL FX-90Q spectrometer in deuteriated toluene and referenced to tetramethylsilane and boron trifluoride etherate, respectively. The IR spectra were recorded on a Perkin-Elmer 297 spectrometer. Mass spectra were obtained with Atlas MS-12 and Consolidated 12-110 instruments at the U.C. Berkeley mass spectroscopy laboratory.

Preparation of $Cp_2Zr(H)BH_3CH_3$ and $Cp_2Zr(D)BD_3CH_3$. Commercially available Cp_2ZrCl_2(1.2 g, 4.1 mmol; Alfa Inorganic) was mixed with $LiBH_3CH_3$[3] (0.36 g, 10 mmol) and stirred for 12 h in either diethyl ether or chlorobenzene. After removal of the solvent by vacuum, the pale yellow residue was sublimed at 60 °C in vacuo and white needle-shaped crystals were collected on a 0 °C cold finger. Alternatively, CpNa (10 mmol) was added to a 1.04-g (5-mmol) sample of $Zr(BH_3CH_3)_4$[3] in diethyl ether. Similar workup procedures yielded the same product. The average yield in both cases is 35%. The deuteriated compound $Cp_2Zr(D)BD_3CH_3$ was made by substituting $LiBH_3CH_3$ with $LiBD_3CH_3$, which in turn was prepared by reacting $LiAlD_4$ with $(CH_3)_3B$.

Table I. Crystal Data and Least-Squares Summary

a, Å[a]	13.775 (3)	μ, cm^{-1}	8.97
b, Å	9.520 (3)	no. of unique data	1387
c, Å	8.816 (2)	no. of non-zero wt data	1365 [$F^2 > \sigma(F^2)$]
cryst syst	orthorhombic	p[b]	0.025
space group	$Cmc2_1$	no. of parameters	116
vol, $Å^3$	1156.1	R (non-zero weighted data)[c]	0.018
d_{calcd}, g/cm^3	1.604	R_w[d]	0.017
Z	4	R (all data)	0.020
temp, °C	23.0	goodness of fit[e]	1.01
empirical formula	$C_{11}H_{17}BZr$	max shift/esd	0.04
F(000)	576	max–min diff map, $e/Å^3$	0.2–0.1
fw	279.15		

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 31 reflections (20° < 2θ < 35°). [b] In the least squares, the assigned weights to the data are $1.0/[\sigma(F)]^2$, derived from $\sigma(F)^2 = [S^2 + (pF^2)^2]$, where S^2 is the variance due to counting statistics and p is assigned a value that adjusts the weights of the stronger reflections such that their weighted residuals are comparable to those of the weak ones. [c] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [e] σ_1 = error in observation of unit weight = $[\sum(w(|F_o| - |F_c|)^2)/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables.

Table II. Positional Parameters with Estimated Standard Deviations

atom	*x*	*y*	*z*
Zr	0	0.29393 (2)	0.250
H^-	0	0.480 (4)	0.222 (5)
B	0.0225 (3)	0.2178 (4)	−0.0260 (5)
C(1)	−0.0562 (7)	0.1871 (7)	−0.1530 (8)
C(2)	0.16155 (21)	0.1800 (4)	0.2682 (10)
C(3)	0.17928 (18)	0.3170 (4)	0.2183 (4)
C(4)	0.15337 (19)	0.4051 (4)	0.3400 (4)
C(5)	0.11813 (20)	0.3263 (3)	0.4569 (4)
C(6)	0.12288 (27)	0.1845 (4)	0.4145 (5)
H(1)	0.011 (6)	0.146 (4)	0.084 (4)
H(2)	0.0219 (26)	0.337 (4)	0.031 (4)
H(3)	0.105 (8)	0.282 (10)	−0.055 (14)
H(4)	−0.112 (4)	0.186 (6)	−0.083 (8)
H(5)	−0.046 (6)	0.106 (12)	−0.192 (9)
H(6)	−0.048 (4)	0.267 (7)	−0.240 (29)
H(7)	0.1622 (28)	0.104 (4)	0.211 (5)
H(8)	0.208 (3)	0.339 (4)	0.113 (5)
H(9)	0.1624 (25)	0.515 (5)	0.348 (4)
H(10)	0.0979 (24)	0.366 (4)	0.550 (4)
H(11)	0.0972 (19)	0.142 (3)	0.474 (4)

X-ray Diffraction. A white, air-sensitive, single-crystal fragment with dimensions 0.18 × 0.12 × 0.65 mm was placed inside a 0.3-mm quartz capillary in an argon-filled drybox; the capillary was sealed to protect the crystal from the atmosphere. A modified Picker FACS-1 automated diffractometer using graphite-monochromated Mo Kα radiation ($\lambda(K\alpha_1)$ = 0.70930 Å, $\lambda(K\alpha_2)$ = 0.71359 Å) was used to collect 5169 θ–2θ scanned intensities; data were collected to a maximum 2θ limit of 55° with a scan width of $(1.50 + 0.693 \tan \theta)°$ on 2θ. Three standard reflections were measured at every 250th reflection; the intensities decayed 3% and were corrected accordingly. The data were corrected for Lorentz and polarization effects and absorption (analytical method);[4] the absorption correction range varied from 1.11 to 1.19. Cell dimensions and other crystal data are given in Table I.

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Table III. Selected Distances (Å) and Angles (deg)[a]

Zr-H$^-$	1.79 (4)	Zr-C(6)	2.461 (3)
Zr-H(1)	2.04 (4)	Zr-B	2.558 (4)
Zr-H(2)	2.00 (3)	B-C(1)	1.585 (8)
Zr-C(2)	2.481 (2)	B-H(1)	1.19 (4)
Zr-C(3)	2.495 (2)	B-H(2)	1.24 (4)
Zr-C(4)	2.493 (2)	B-H(3)	1.32 (10)
Zr-C(5)	2.464 (2)	Cp-Zr	2.177
H$^-$-Zr-B	98.6 (14)	B-Zr-Cp	102.6
Zr-B-C(1)	130.4 (4)	B-Zr-Cp′	116.9
H$^-$-Zr-Cp	95.7	Cp-Zr-Cp′	137.1

[a] Cp represents the center of the cyclopentadienyl ring C(2)-C(6); Cp′ represents the equivalent group at $-x$, y, z.

Table IV. Nuclear Magnetic Resonance Data (ppm) for $Cp_2Zr(H)BH_3CH_3$

nucleus	chem shift[a]
^1H	+5.61 (10 H, s), +4.16 (1 H, s), +0.51 (3 H, s), −1.20 (3 H, br, quart)
^{11}B	+20.2 (quart)

[a] Shifts are referenced to Me_4Si and $BF_3{\cdot}OC_2H_5$ for ^1H and ^{11}B, respectively. Positive sign indicates a downfield shift.

Table V. Infrared Spectroscopic Data (cm^{-1}) for $Cp_2Zr(H)BH_3CH_3$ and $Cp_2Zr(D)BD_3CH_3$[a]

compd	freq
$Cp_2Zr(H)BH_3CH_3$	2388 s, 2240 w, 2078 w, 1903 s, 1850 m, 1810 sh, 1720 w, 1610 m, 1595 sh, 1290 w, 1260 w, 1125 s, 1065 w, 1010 s, 993 w, 855 w, 830 sh, 808 s
$Cp_2Zr(D)BD_3CH_3$	1775 m, 1720 m, 1610 m, 1290 w, 1260 w, 1205 w, 1150 m, 1115 w, 1065 w, 1030 s, 1010 s, 972 w, 910 w, 830 sh, 808 s, 735 m, 720 m

[a] Nujol mull in KBr disks.

The Zr atom position was located with the use of three-dimensional Patterson maps; subsequent least-squares refinements and electron density maps revealed the locations of the other atoms. The structure was refined by full-matrix least squares by using anisotropic thermal parameters on the non-hydrogen atoms and isotropic thermal parameters on the hydrogen atoms. The atoms of the methyltrihydroborato group are disordered across a mirror plane and were placed in general positions of the space group with $^1/_2$ occupancy factors. Scattering factors[5] were adjusted for anomalous dispersion. The H$^-$ scattering factors were used for the hydride ion, and neutral-H values were used for the other hydrogen atoms. The positional parameters of H(3) would not converge; these parameters were not varied in the final refinements. The statistical results of the least squares are shown in Table I, the positional parameters in Table II, and distances and angles in Table III.

Results and Discussion

$Cp_2Zr(BH_4)_2$ has been isolated from the reaction of Cp_2ZrCl_2 with $LiBH_4$. $Cp_2Zr(H)BH_4$ can be obtained as the product of a bridge-cleavage reaction of $Cp_2Zr(BH_4)_2$ with $(CH_3)_3N$.[1] We have been unable to isolate $Cp_2Zr(BH_3CH_3)_2$ and form the hydride directly by the reaction of Cp_2ZrCl_2 with $LiBH_3CH_3$. The hydride does not result from the thermal decomposition of $Cp_2Zr(BH_3CH_3)_2$ during sublimation since similar NMR and IR spectra (see Tables IV and V) were obtained before and after sublimation. In contrast, both $Cp_2U(BH_3CH_3)_2$[6] and $Cp_2U(BH_4)_2$[7] have been prepared and found to contain only tridentate methyltrihydroborato and tetrahydroborato groups, respectively.

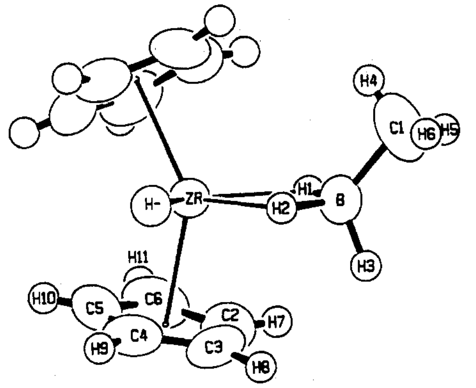

Figure 1. ORTEP drawing of $(C_5H_5)_2Zr(H)BH_3CH_3$. Only one conformation of the disordered methyltrihydroborate group is shown.

The mass spectrum of $Cp_2Zr(H)BH_3CH_3$ consists of three groups of proportional peaks that correspond to the presence of five zirconium and two boron isotopes. The largest group peaks at m/e 249 (relative intensity 100), which is expected for the fragment $Cp_2{}^{90}Zr^{11}BH_3CH_3{}^+$; metal tetrahydroborates and related compounds do not show a very strong parent ion.[1] The other two groups peak at m/e 235 and 221 (relative intensities 70 and 19, respectively), corresponding to the loss of a CH_3 and a BH_3CH_3 fragment, respectively.

The ^1H NMR spectrum of $Cp_2Zr(H)BH_3CH_3$ shows chemical shifts very similar to those of $Cp_2Zr(H)BH_4$, and the deuteriated compound $Cp_2Zr(D)BD_3CH_3$ gives the expected spectrum with marked decreases in intensities of the hydride and BH_3 peaks. The multiplicities of the BH_3 peak and the ^{11}B spectrum clearly indicate that the three hydrogens bonded to the boron atom are equivalent in solution; no detectable difference can be observed at a temperature of −60 °C. Dynamic interchange of Cp and BH_3 protons has also been shown to exist.[8]

The IR spectrum is rather complicated and shows a great similarity to the spectrum of $Cp_2TiBH_3CH_3$ (prepared by a similar reaction between Cp_2TiCl_2 and $LiBH_3CH_3$) except for the presence of a broad peak at 1595 cm^{-1}. This band is assigned as the Zr-hydride stretch, which agrees with those found in $Cp_2Zr(H)BH_4$ (1620 cm^{-1})[9] and $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (1555 cm^{-1}).[10] Upon deuteriation this band is shifted to 1150 cm^{-1} (ν(M-H)/ν(M-D) = 1.387). Comparison of the IR data for both $Cp_2Zr(H)BH_3CH_3$ and $Cp_2TiBH_3CH_3$ with those for Cp_2TiBH_4, which contains only double hydrogen-bridge bonds,[11] suggests that the methyltrihydroborato group is doubly hydrogen bridged in these compounds. The bidentate ligation in $Cp_2Zr(H)BH_3CH_3$ has been confirmed by an X-ray crystal structure determination.

The zirconium atom is at the center of a distorted tetrahedron consisting of the centers of two cyclopentadienyl rings, a hydride ion, and the boron atom of the methyltrihydroborato group and is bridge-bonded to the boron atom via two hydrogen atoms (see Figure 1). The zirconium atom and hydride ion are in special positions on the mirror plane. The cyclopentadienyl rings bonded to the zirconium atom are across the mirror plane from each other and therefore in a rigorously eclipsed configuration when viewed down the a axis. The methyltrihydroborato group is disordered across the mirror plane and is randomly located on one side of the mirror plane or the other.

The zirconium-terminal hydrogen distance of 1.79 Å is considerably longer than that found in $(\eta^5\text{-}C_8H_{11})Zr(H)(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane).[12] Such a difference probably cannot be explained by steric crowding alone as the average Zr-C and the Zr-ring centroid distances in $Cp_2Zr(H)BH_3CH_3$ are both shorter than those found in comparable compounds such as Cp_2ZrF_2[13] and Cp_2ZrCl_2.[14] However, it is in good

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agreement with the Zr–H bond lengths found in $(\eta\text{-}C_5Me_5)Zr(\eta\text{-}C_8H_8)H$ (1.81 and 1.78 Å)[2c] and $\{ZrH(\mu\text{-}H)(\eta\text{-}C_5H_4Me)_2\}_2$ (1.78 Å);[15] it is also consistent with the covalent radii of the elements[16] (the Bragg–Slater radii of hydrogen and zirconium are 0.25 and 1.55 Å, respectively).[17] The Zr–B distance of 2.558 Å is indicative of a bidentate methyltrihydroborato group as compared to 2.335 and 2.31 Å in the triply hydrogen bridged $Zr(BH_3CH_3)_4$[2] and $Zr(BH_4)_4$, respectively.[18]

We have been unable to isolate $Cp_2Zr(BH_3CH_3)_2$ by the synthetic route with which $Cp_2U(BH_3CH_3)_2$ is prepared. This may be due to the smaller ionic radius of Zr(IV) (0.19 Å smaller than that of U(IV)),[19] which results in a larger coordination number about U(IV) as shown by the difference in molecular structure between $Zr(BH_4)_4$ and $U(BH_4)_4$.[20] Moreover, we have also been unable to isolate the compound $Cp_2U(H)BH_3CH_3$.

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Supplementary Material Available: Tables of thermal parameters, additional distances and angles, the least-squares plane, and the calculated powder pattern and additional ORTEP drawings (6 pages); a table of observed structure factors and their discrepancies from the calculated values (6 pages). Ordering information is given on any current masthead page.

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Comparison of Dative and Covalent Metal–Metal Bonds: Structures of the Isomers $(Me_3P)(OC)_4OsRe(CO)_4(Br)$ and $(Br)(Me_3P)(OC)_3OsRe(CO)_5$

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Recent work from this laboratory has demonstrated that neutral 18-electron organometallic compounds can act as ligands.[1–4] Structural studies appeared to indicate that the donor–acceptor metal–metal bonds in the resulting complexes were somewhat longer than the covalent bonds reported in the literature between the same metals. In each case, however, the molecules that were compared were very different and it was not clear if the small differences in the metal–metal bond lengths could be attributed to the electronic nature of the bond or to the various ligand influences within each molecule.

Here we report the synthesis and structure of the isomers $(Me_3P)(OC)_4OsRe(CO)_4(Br)$ and $(Br)(Me_3P)(OC)_3OsRe(CO)_5$. These structures allow for the first time a comparison of a dative and a covalent metal–metal bond in molecules where the changes in ligand influences have been kept to a minimum.

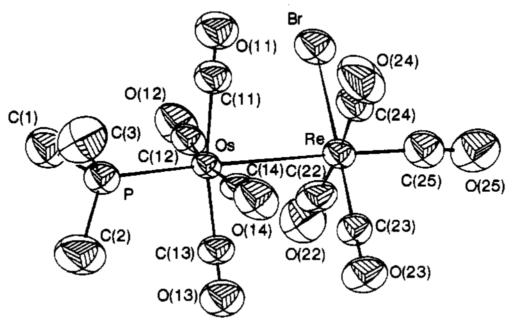

Figure 1. Molecular structure of $(Me_3P)(OC)_4OsRe(CO)_4(Br)$ (**1**). Ellipsoids enclose 50% probabilities; hydrogen atoms are deleted here and in Figure 2.

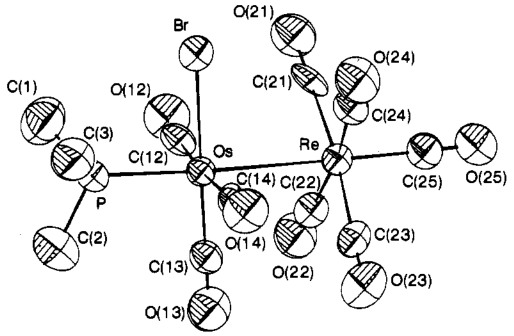

Figure 2. Molecular structure of $(Br)(Me_3P)(OC)_3OsRe(CO)_5$ (**2**).

Experimental Section

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Hexane and dichloromethane were distilled under nitrogen from potassium and P_2O_5 respectively, before use. Literature methods were used to prepare $[Re(CO)_4(Br)]_2$[5] and $Os(CO)_4(PMe_3)$.[6] The hydride $Re(CO)_5(H)$ was prepared by the reduction of $Re(CO)_5(Br)$ with powdered zinc in acetic acid; a preparation similar to this has been reported by Shapley and co-workers.[7]

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer, mass spectra on a Hewlett-Packard 5985 GC-MS spectrometer, and NMR spectra on a Bruker WM400 spectrometer (operating frequencies: 400 MHz for ^1H, 100.6 MHz for ^{13}C, and 161.96 MHz for ^{31}P). In order to obtain a good signal to noise ratio for the ^{13}C NMR spectra, overnight accumulation of transients was employed or ^{13}C-enriched samples were used. (The enrichment by ^{13}CO of $Re(CO)_5(Br)$[8] and $Os(CO)_4(PMe_3)$[2] has been described.) The assignments of ^{13}C NMR resonances reported below are made with reference to Figures 1 and 2. The ^{31}P NMR spectra are referenced to external 85% H_3PO_4 (downfield positive). The microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of $(Me_3P)(OC)_4OsRe(CO)_4(Br)$. A 100-mL round-bottom flask (fitted with a Teflon valve) charged with $[Re(CO)_4(Br)]_2$ (0.096 g, 0.127 mmol), $Os(CO)_4(PMe_3)$ (0.096 g, 0.254 mmol), and CH_2Cl_2 (15 mL) was cooled to −196 °C and evacuated; the solution was degassed with two freeze–pump–thaw cycles. The solution was then heated, with stirring, at 50 °C for 2.5 h. After this period the solution was cooled, filtered through Celite to a Schlenk flask, and concentrated to ~5 mL. Hexane (10 mL) was added, and the resultant solution stored at −15 °C overnight whereupon pale yellow crystals formed. The mother solution was removed, and the crystals were washed with hexane and dried on the vacuum line.

The air-stable product, $(Me_3P)(OC)_4OsRe(CO)_4(Br)$ (0.15 g, 78%), was pure by infrared spectroscopy. The analytical sample was obtained by recrystallization from CH_2Cl_2–hexane. IR (CH_2Cl_2): $\nu(CO)$ 2115

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