the LF matrix was checked against the weak-field matrix of McFarlane[3] by setting $\zeta = 0$, the spin–orbit coupling matrix was checked against the Eisenstein matrix[30] by setting $K$ and $K' = 0$, and the resulting $g$ values from the external magnetic field

matrix were checked with the Lande formula for $g$ values of the free ion[18] by setting $10Dq = K = K' = 0$. In the calculations appropriate for $[\text{Cr(bpy)}_3]^{3+}$ the Racah parameters $B$ and $C$ were reduced from their free-ion values of 1030 and 3850 cm$^{-1}$,[18] respectively, by an orbital reduction factor $\beta = E(^2E_{complex})/E(^2E_{free\ ion}) = 0.71$.[20]

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# Notes

Contribution from the Department of Chemistry, D-006, University of California, San Diego, La Jolla, California 92093

## Perhalogenated Tetraphenylhemins: Stable Catalysts of High Turnover Catalytic Hydroxylations

Teddy G. Traylor* and Shinji Tsuchiya

Recent interest in biochemical, biomimetic, and synthetic hydroxylation reactions[1–3] that are catalyzed by metalloporphyrins has prompted us to seek more robust catalysts. We recently reported tetraphenylhemin derivatives bearing, as 2,6-substituents on the phenyl rings, groups that are both electronegative and bulky.[4,5] Of these, iron(III) tetrakis(2,6-dichlorophenyl)porphyrin chloride (1$^+$Cl$^-$) has become a widely used catalyst for epoxidation reactions.[5–8] However, neither this compound nor the iron(III) tetrakis(2,6-ditrifluoromethylphenyl)porphyrin[9] are sufficiently robust to afford high turnover catalyzed hydroxylation without catalyst loss.[4] We have therefore turned to further halogenation of this compound to provide iron porphyrins that are resistant to attack by the strong oxidizing agents generated as intermediates. This strategy has been successful. We describe here a simple bromination that converts 1-Zn to its octabromo derivative, affording a very robust iron porphyrin catalyst, Fe$^{III}$88TPP, in good yield.

### Experimental Section

The zinc tetrakis(2,6-dichlorophenyl)porphyrin complex (1-Zn) (1 g, 0.001 M)[4,10] was dissolved in carbon tetrachloride (100 mL), and *N*-bromosuccinimide (1.85 g, 0.01 M) was added to this solution.[11] This solution was refluxed under air for 5 h and allowed to stand at room temperature for 2 h. The reaction mixture was reduced to dryness and the resulting black solid chromatographed on alumina, eluting with chloroform. The first moving fraction was collected. Evaporation of solvent yielded 1.1 g of the brominated zinc complex (2-Zn) (yield 71%). The 300-MHz NMR spectrum of this compound consisted of a complex phenyl region at 7.2–7.8 ppm but no peaks due to pyrrole protons.[12] The UV–visible spectrum is listed in Table I along with other spectra.

The zinc complex (1 g) was dissolved in 100 mL of dichloromethane and 10 mL of trifluoroacetic acid was added. This mixture was stirred for 5 h and poured into ice. The organic layer, which slowly separated, was removed and washed with water and with saturated aqueous sodium bicarbonate. The evaporation of the solvent gave the desired porphyrin

**Table I.** UV–Visible Spectra of Derivatives of 88TPP (2)

| | $\lambda_{max}$, nm ($\epsilon^a$) | | | |
|---|---|---|---|---|
| porphyrin | | 462 (100) | 557 (7) | 598 (2.7) | 603 (sh) |
| Zn complex | | 468 (100) | 602 (6) | 600 (sh) | |
| Fe$^+$Cl$^-$ complex | 400 (84) | 453 (100) | 580 (sh) | | |
| Fe$^+$OH$^-$ complex | | 424 (100) | 495 (87) | 600 (14) | |

$^a$All extinction coefficients are relative to the Soret maximum in the species and are not absolute nor related to other derivatives.

(0.75 g). This porphyrin was purified by alumina column chromatography using chloroform as solvent. Again the NMR was characterized by a complex phenyl proton pattern at 7.2–7.8 ppm. The parent peak in the mass spectrum consisted of at least 16 lines centered at 1521, in agreement with the calculated $M_r$. The UV-visible spectrum listed in Table I shows a Soret absorption at 462 nm. This is 48-nm red shifted from the starting octachloroporphyrin, in good agreement with the approximately 6 nm/Br shift found by Callot for the mono- to tetra-brominated tetraphenylporphyrins. The porphyrin was converted to the Fe(III) derivative, 2$^+$Cl$^-$, by the standard FeBr$_2$/DMF procedure,[13] followed by purification from unreacted porphyrin by alumina chromatography. The UV–visible spectrum is listed in Table I. The NMR of 2$^+$Cl$^-$ consisted of absorbances at 14.42, 14.01 (meta protons), and 7.48 (para) ppm. This compares with 13.98, 12.67 (meta), 8.1 (para), and 80.5 (pyrrole protons) ppm for 1$^+$Cl$^-$, indicating the absence of pyrrole protons in 2$^+$Cl$^-$.

### Results and Discussion

The remarkable stability of the octabromooctachlorohemin toward destruction during catalyzed hydroxylation is demonstrated by the following experiments. Portions of a solution containing 1 M norbornane and 0.06 M pentafluoroiodosylbenzene[4] (as a suspension) were treated separately with tetraphenylhemin chloride, 1$^+$Cl$^-$, and 2$^+$Cl$^-$. In the first case the solution instantly bleached and little or no oxidant dissolved. With 1$^+$Cl$^-$ about 75% hemin destruction was accompanied by dissolution of the oxidant and about 40% yield of 2-norborneols. With 2$^+$Cl$^-$, a 75% yield of norborneols was obtained and no hemin loss was observed. Diluted spectra of the starting and final solutions had the same Soret absorbance at 453 nm. In another comparison a solution of 0.3 M cholestane (Aldrich) and 10$^{-4}$ M hemin (either 2$^+$Cl$^-$ or tetrakis(pentafluorophenyl)hemin chloride (Aldrich)) was shaken with 0.06 molar equiv of PFIB until the solid dissolved or bleaching occurred. With 2$^+$Cl$^-$, 40% loss of the Soret band occurred whereas the tetrakis(pentafluorophenyl)hemin chloride was completely bleached. At higher hemin and substrate concentrations there was no loss of 2$^+$Cl$^-$ and about 50% loss of the fluorinated hemin.

Epoxidation of 4,4-dimethyl-1-pentene using 2$^+$Cl$^-$ under the conditions that resulted in complete conversion to *N*-alkylhemin with 1$^+$Cl$^-$[8] gave no change in the spectrum of 2$^+$Cl$^-$. Therefore it is much less prone to "suicide labeling" than are other hemins.

In the soluble system (CH$_2$Cl$_2$, CF$_3$CH$_2$OH, H$_2$O)[14] where tetraphenylhemin, tetramesitylhemin, and 1$^+$Cl$^-$ are destroyed at

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(9) Tsuchiya, S., unpublished work.
(10) Bromination of the free porphyrin was less successful.
(11) This is a variation of the method of: Callot, H. J. *Bull. Soc. Chim. Fr.* **1974**, 1492.
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$10^{-5}$ M in the presence of 1 M norbornane, good first-order disappearance of oxidant was observed with $2^+Cl^-$, and hemin loss was slight although the spectrum changed somewhat.

These observations show that $2^+Cl^-$ ($Fe^{III}88TPP$) is an extraordinarily stable catalyst for hydroxylation or epoxidation. The simplicity and high yield of the synthesis of $2^+Cl^-$ 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]

**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.

(15) Improved syntheses of **1P** yield will be reported elsewhere.
(16) Dolphin and Nakano (Dolphin, D.; Nakano, T., private communication) have octachlorinated $1^+Cl^-$ to produce a hemin with properties similar to those of $2^+Cl^-$.

Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720

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

Wing K. Kot, Norman M. Edelstein,* and Allan Zalkin*

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 = $\eta^5$-$C_5H_5$).[1] Other zirconium hydrides have also been synthesized by reacting $LiAlH_4$, $LiAl(O$-$t$-$C_4H_9)_3H$, $LiBH_4$, 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

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**Table I.** Crystal Data and Least-Squares Summary

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

$^a$ Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo K$\alpha$ components of 31 reflections ($20°$ $< 2\theta < 35°$). $^b$ 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. $^c R = \sum(|F_o| - |F_c|)/\sum|F_o|$. $^d R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. $^e \sigma_1$ = 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) |

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 $(CH_3)_3B$.

**X-ray Diffraction.** A white, air-sensitive, single-crystal fragment with dimensions $0.18 \times 0.12 \times 0.65$ 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 K$\alpha$ radiation ($\lambda$(K$\alpha_1$) $= 0.709\,30$ Å, $\lambda$(K$\alpha_2$) = $0.713\,59$ Å) was used to collect 5169 $\theta$–$2\theta$ scanned intensities; data were collected to a maximum $2\theta$ limit of 55° with a scan width of $(1.50 + 0.693 \tan \theta)°$ on $2\theta$. 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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