Syntheses and Characterization of Dichlorozirconium Porphyrin Complexes and Their Novel Organometallic Derivatives. X-ray Structure of $Zr(TPP)Cl_2(THF)$[1]

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Introduction

The chemistry of early transition metal porphyrin complexes, especially, that of the second- and third-row metal complexes has not been developed much due in part to their high oxophilicity.[2] We have been interested in exploring zirconium and hafnium porphyrin complexes because they may show a rich organometallic chemistry as zirconocene derivatives do.[3] The key entry to the organometallic zirconium porphyrin complexes would be Zr(porphyrin)Cl_2, analogous to $ZrCp_2Cl_2$. The dichloride complex may be converted to organometallic σ-complexes such as dialkyl complexes by the reactions with alkyllithium or Grignard reagents. It may also form organometallic π-complexes by replacing the two chlorides with a cyclooctatetraenyl dianion or a dicarbollide dianion. Indeed, we have succeeded in preparing Zr(por)Cl_2 (por = OEP, TPP)[4] and their organometallic derivatives Zr(TPP)Me_2 and Zr(OEP)(η^5-$C_2B_9H_{11}$). We have presented[1] the preliminary results on their syntheses and characterization by spectroscopy but have been unable to grow X-ray-quality crystals of either of the organometallic complexes until recently. When we finished the structural characterization of Zr(OEP)(η^5-$C_2B_9H_{11}$) by X-ray crystallography, however, Arnold and coworkers published[5] the synthesis and characterization of Zr(OEP)Cl_2 and several organometallic complexes derived from it, including Zr(OEP)$(CH_2SiMe_3)_2$[5a] and Zr(OEP)(η^5-$C_2B_9H_{11}$).[5b] Here we present our results on the syntheses and characterization of Zr(por)Cl_2 (por = OEP, TPP), Zr(TPP)Me_2, and Zr(OEP)(η^5-$C_2B_9H_{11}$) and the X-ray structure of Zr(TPP)Cl_2(THF).

Experimental Section

Chemicals. All chemicals were of reagent grade and were used without further purification except as noted below. Argon was purified by passage through successive columns of activated molecular sieves 13X (Aldrich) and Ridox (Fisher). $ZrCl_4(THF)_2$,[6] $Li_2(OEP)$,[7] and $Tl_2(C_2B_9H_{11})$[8] were prepared by literature procedures. All solvents were distilled from their sodium benzophenone ketyl solutions (toluene, THF, and hexanes) or from P_2O_5 (CH_2Cl_2) under an atmosphere of nitrogen.

Methods and Instruments. All manipulations of oxygen- and water-sensitive materials were performed either in a glovebox of a Vacuum Atmospheres HE-63-P Dri-Lab with an HE 493 Dri-Train under a nitrogen atmosphere or in Schlenkware under purified argon. UV-visible spectra were recorded on a Hewlett-Packard 8542A spectrometer. ^1H and $^{11}B\{^1H\}$ NMR spectra were obtained on a Bruker AM 300 spectrometer. In $^{11}B\{^1H\}$ NMR spectra, chemical shifts are referenced to external $BF_3 \cdot Et_2O$ at 0 ppm. Infrared spectra were recorded on a Bomem Michelson 100 spectrometer.

Syntheses. (a) Dichloro(octaethylporphyrinato)zirconium(IV), (OEP)$ZrCl_2$ (1a). $ZrCl_4(THF)_2$ (0.661 g, 1.75 mmol) and $[Li(THF)_4][Li(OEP)]$[7] (1.326 g, 1.59 mmol) were dissolved in toluene (ca. 200 mL), and the solution was heated at reflux under an inert atmosphere. The progress of the reaction was monitored by UV-vis spectroscopy and TLC. After 2 h of reflux, the solid was filtered off and washed with CH_2Cl_2. The filtrate was concentrated and allowed to cool to -20 °C overnight. A dark red solid was filtered off, washed with hexanes, and dried under vacuum. Yield: 0.877 g (79%). Anal. Calcd for $C_{36}H_{44}N_4ZrCl_2$: C, 62.21; H, 6.39; N, 8.06. Found: C, 61.88; H, 6.29; N, 8.30. UV-vis (CH_2Cl_2), λ_{max}, nm (log ϵ): 332 (3.59), 378 (4.68), 400 (5.31), 484 (3.31), 528 (3.91), 564 (4.03). ^1H NMR (300 MHz, $CDCl_3$): δ 10.63 (s, meso H), 4.22 (m, CH_2), 1.91 (t, J_{HH} = 7.5 Hz, CH_3). IR (KBr), cm^{-1}: 2966 (s), 2931 (s), 2870 (m), 1627 (m), 1459 (s), 1374 (m), 1269 (w), 1145 (w), 1059 (s), 1016 (s), 961 (s), 855 (w), 744 (w), 697 (w).

(b) Dichloro(*meso*-tetraphenylporphyrinato)zirconium(IV), (TPP)$ZrCl_2$ (1b).[9] **1b** was synthesized in 83% yield by the same procedure as for **1a** using the dilithium salt of *meso*-tetraphenylporphyrin, which was prepared by the same method as for $[Li(THF)_4][Li(OEP)]$.[7] Anal. Calcd for $C_{44}H_{28}N_4ZrCl_2$: C, 68.20; H, 3.65; N, 7.23. Found: C, 68.58; H, 3.33; N, 7.20. UV-vis (CH_2Cl_2), λ_{max}, nm (log ϵ): 398 (4.96), 418 (5.98), 502 (3.75), 540 (4.62), 574 (3.65). ^1H NMR (300 MHz, $CDCl_3$): δ 9.11 (s, pyrrole H), 8.42 (s, 4 *o*-H), 8.08 (t, J_{HH} = 7.3 Hz, 4 *p*-H), 7.84 (s, 12 H). IR (KBr), cm^{-1}: 3045 (w), 1611 (s), 1486 (m), 1441 (m), 1339 (s), 1204 (w), 1074 (m), 998 (s), 806 (s), 754 (s), 703 (s). Recrystallization of **1b** from THF/dichloromethane/heptane gave the THF adduct Zr(TPP)Cl_2(THF) (**1c**). ^1H NMR (300 MHz, $CDCl_3$): δ 9.08 (s, pyrrole H), 8.44 (s, 4 *o*-H, fwhm[4] = 17 Hz), 8.04 (d, J_{HH} = 7.3 Hz, 4 *p*-H, fwhm = 18 Hz), 7.82 (s, 8 H, fwhm = 21 Hz), 7.78 (s, 4 *o'*-H, fwhm = 19 Hz), 3.71 (m, 4 H, THF), 1.84 (m, 4 H, THF).

(c) Dimethyl(*meso*-tetraphenylporphyrinato)zirconium(IV), (TPP)$ZrMe_2$ (2). To the suspension of (TPP)$ZrCl_2$ (0.211 g, 0.272 mmol) in toluene (ca. 20 mL) was added slowly 0.39 mL of methyllithium (0.55 mmol, 1.4 M in diethyl ether). The reaction mixture was stirred at room temperature for 1 h and then filtered. The filtrate was concentrated and allowed to cool to -20 °C overnight. The purple crystalline solid was filtered off, washed with hexanes, and dried under vacuum. Yield: 0.150 g (75%). Anal. Calcd for $C_{46}H_{34}N_4Zr$: C, 75.26; H, 4.68; N, 7.63. Found: C, 74.93; H, 5.06; N, 7.18. UV-vis (toluene), λ_{max}, nm (log ϵ): 414 (5.44), 512 (3.46), 546 (4.17), 580 (3.29), 628 (2.82).[10] ^1H NMR (300 MHz, C_6D_6): δ 9.01 (s, pyrrole H), 8.28 (s, 4 H, fwhm = 18 Hz), 7.91 (s, 4 H, fwhm = 18 Hz), 7.47 (s, 12 H, fwhm = 20 Hz), -3.26 (s, CH_3). IR (KBr), cm^{-1}: 3051 (w), 1596 (w), 1483 (w), 1440 (w), 1334 (m), 1202 (w), 1176 (w), 1071 (m), 997 (s), 803 (s), 751 (s), 727 (s), 703 (s), 659 (w), 618 (w), 573 (w).

(d) (η^5-1,2-Dicarbollyl)(octaethylporphyrinato)zirconium(IV), (η^5-1,2-$C_2B_9H_{11}$)Zr(OEP) (3). (OEP)$ZrCl_2$ (50 mg, 0.072 mmol) and $Tl_2C_2B_9H_{11}$ (60 mg, 0.11 mmol) were placed in a 50-mL round-bottom flask to which was added THF (ca. 20 mL). The resulting suspension was stirred at room temperature for 48 h under an inert atmosphere. The reaction mixture was then filtered, and the filtrate was evaporated to dryness in vacuo. In order to remove the unreacted (OEP)$ZrCl_2$, the residue was redissolved in toluene and the solution was passed through a short silica gel column using toluene and CH_2Cl_2. While (OEP)Zr($C_2B_9H_{11}$) was readily eluted with toluene or CH_2Cl_2 (R_f = 0.5 on silica TLC using toluene as an eluent), (OEP)$ZrCl_2$ was not. The eluted solution was concentrated and allowed to cool to -20 °C overnight. The red

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(1) Preliminary results of this work have been presented at the 68th Annual Meeting of the Korean Chemical Society, Chang-Won, Korea, Oct 25-26, 1991.

(2) Buchler, J. W. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. 1, pp 389-483.

(3) Cardin, D. J.; Lappert, M. F.; Rarson, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood Ltd.: Chichester, England, 1986.

(4) Abbreviations: TPP = 5,10,15,20-tetraphenylporphyrin dianion; OEP = octaethylporphyrin dianion; fwhm = full width at half-maximum.

(5) (a) Brand, H.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 2266-2267. (b) Arnold, J.; Johnson, S. E.; Knobler, C. B.; Hawthorne, M. F. *Ibid.* **1992**, *114*, 3996-3997.

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(8) Spencer, J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, *1178*-1179.

(9) Zr(TPP)Cl_2 was first reported by Berezin and Lomova (Berezin, B. D.; Lomova, J. N. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1981**, *26*, 203-207); however, their work lacks the characterization of the compound.

(10) One of the reviewers pointed out that the band at 628 nm may be due to a minor impurity such as a chlorin complex. We cannot completely rule out the possibility at the moment although the elemental analysis was satisfactory and the NMR spectrum shows only one compound.

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Table I. Crystallographic Data for **1c**

formula	$C_{48}H_{36}N_4Cl_2OZr$	temp, °C	23
fw	846.97	d_{calcd}, g cm^{-3}	1.433
space group	$P\bar{1}$(No. 2)	λ(Mo Kα), Å	0.709 26
a, Å	11.5774 (9)	linear abs coeff, cm^{-1}	4.54
b, Å	12.3997 (11)	transm coeff	0.961–0.998
c, Å	15.5891 (13)	2θ limits, deg	$3.0 \le 2\theta \le 45.0$
α, deg	102.595 (7)	no. of data collected	5431
β, deg	106.545 (7)	no. of unique data with $I > 3\sigma(I)$	3740
γ, deg	105.228 (7)	$R(F)^a$	0.037
V, Å^3	1963.5 (3)	$R_w(F)^b$	0.040
Z	2		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o^2)$; $\sigma(F_o^2) = [\sigma(I) + (pI)^2]^{1/2}$.

precipitates of (OEP)Zr($C_2B_9H_{11}$) were filtered off and dried under vacuum (yield 34 mg, 64%). Anal. Calcd for $C_{38}H_{55}N_4B_9Zr$: C, 60.33; H, 7.34; N, 7.41. Found: C, 60.06; H, 6.94; N, 7.61. UV–vis (CH_2Cl_2), λ_{max}, nm (log ε): 322 (3.64), 382 (4.84), 400 (5.41), 482 (3.22), 528 (3.96), 566 (4.10). ^1H NMR (300 MHz, $CDCl_3$): δ 10.65 (s, meso H), 4.23 (m, CH_2), 1.90 (t, J_{HH} = 7.5 Hz, CH_3), –2.83 (s, carborane CH). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ 0.21, –5.16, –11.52, –14.30, –22.75. IR (KBr), cm^{-1}: 2966 (s), 2931 (s), 2870 (m), 2547 (vs, BH), 1720 (w), 1635 (w), 1456 (s), 1372 (m), 1312 (w), 1268 (m), 1215 (w), 1147 (m), 1110 (w), 1056 (s), 1016 (s), 977 (s), 957 (s), 916 (m), 857 (m), 805 (w), 741 (m), 702 (m).

X-ray Crystal Structure Determination. X-ray-quality crystals of Zr(TPP)Cl_2(THF) (**1c**) were obtained by recrystallization of **1b** from THF/dichloromethane/heptane. A crystal was mounted in a sealed capillary tube with the mother liquor on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Unit cell parameters were determined by least-squares refinement of 25 reflections. Crystal data for **1c** are summarized in Table I. Data collection was carried out at room temperature. The intensities of three standard reflections, measured every 3 h of X-ray exposure, showed no systematic changes. All the calculations were carried out with the Enraf-Nonius MolEN package.[11] The intensity data were corrected for Lorentz and polarization effects, and empirical absorption corrections (DIFABS)[12] were also applied. The structures were solved by a combination of Patterson and difference Fourier methods and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms (except for the solvate molecules) were calculated (C–H = 0.95 Å) and were included as fixed contributions to the structure factors. Each hydrogen atom was assigned an isotropic thermal parameter 1.2 times that of the atom to which it is attached. The final cycle of refinement of F, including 3740 observations and 505 variables, converged to the agreement indices given in Table I. Scattering factors for H were obtained from Stewart et al.,[13] and those for other atoms were taken from ref 14. Positional and equivalent isotropic thermal parameters for **1c** are listed in Table II.

We also determined the X-ray structure of **3**, which is essentially the same as the one reported by Arnold et al.[5b] The structural parameters of our structure have slightly larger estimated standard deviations. Crystallographic data for (η^5-1,2-$C_2B_9H_{11}$)Zr(OEP) (**3**): triclinic, $P\bar{1}$, a = 10.951 (3) Å, b = 12.679 (5) Å, c = 14.848 (5) Å, α = 83.54 (3)°, β = 85.36 (2)°, γ = 78.37 (3)°, V = 2003 (1) Å^3, Z = 2, d_{calcd} = 1.256 g cm^{-3}, R = 0.058 and R_w = 0.066 for 3759 absorption corrected reflections with $I > 3\sigma(I)$.

Results and Discussion

The key precursors to the organometallic zirconium porphyrin complexes Zr(por)Cl_2 (por = OEP, TPP)[9] were prepared by the reactions of $ZrCl_4(THF)_2$ with the lithium salts of the corresponding porphyrins in THF. Brand and Arnold[5a] recently reported the synthesis of the OEP complex using $ZrCl_4(THT)_2$ (THT = tetrahydrothiophene). The dichlorozirconium porphyrins were characterized by various spectroscopic means and elemental analyses. NMR spectra of the OEP complex **1a** show that the methylene protons of the ethyl groups are diastereotopic, which indicates that the environment of the two sides of the porphyrins are different; therefore, the two chloride ions are present on the same side of the porphyrin plane. The cis geometry of the two chloride ions in the TPP complex has been confirmed by X-ray crystallography.

Table II. Positional and Equivalent Isotropic Thermal Parameter for Non-Hydrogen Atoms of **1c**

atom	x	y	z	B_{eq},^{a} Å^2
Zr	0.24497 (4)	0.25279 (4)	0.75191 (3)	2.610 (9)
Cl1	0.1402 (1)	0.0702 (1)	0.61487 (8)	4.08 (3)
Cl2	0.1144 (1)	0.1356 (1)	0.82520 (8)	4.04 (3)
O	0.0376 (3)	0.2623 (3)	0.6731 (2)	3.75 (8)
N1	0.3931 (3)	0.2825 (3)	0.8944 (2)	2.81 (9)
N2	0.4124 (3)	0.2226 (3)	0.7169 (2)	2.80 (9)
N3	0.2809 (3)	0.3753 (3)	0.6656 (2)	2.83 (9)
N4	0.2443 (3)	0.4225 (3)	0.8405 (2)	2.90 (9)
C1	0.3804 (4)	0.3278 (4)	0.9802 (3)	2.9 (1)
C2	0.4685 (4)	0.3071 (4)	1.0539 (3)	3.7 (1)
C3	0.5362 (4)	0.2517 (4)	1.0159 (3)	3.6 (1)
C4	0.4870 (4)	0.2336 (4)	0.9166 (3)	3.0 (1)
C5	0.5286 (4)	0.1744 (4)	0.8513 (3)	3.5 (1)
C6	0.4888 (4)	0.1644 (4)	0.7562 (3)	3.2 (1)
C7	0.5267 (5)	0.1006 (4)	0.6874 (3)	4.2 (1)
C8	0.4756 (4)	0.1210 (4)	0.6067 (3)	4.0 (1)
C9	0.4086 (4)	0.2004 (4)	0.6237 (3)	3.2 (1)
C10	0.3565 (4)	0.2544 (4)	0.5618 (3)	3.1 (1)
C11	0.3104 (4)	0.3444 (4)	0.5857 (3)	3.3 (1)
C12	0.2917 (5)	0.4237 (4)	0.5335 (3)	4.1 (1)
C13	0.2553 (5)	0.5043 (4)	0.5819 (3)	4.0 (1)
C14	0.2456 (4)	0.4728 (4)	0.6631 (3)	3.2 (1)
C15	0.2035 (4)	0.5322 (4)	0.7289 (3)	3.3 (1)
C16	0.1988 (4)	0.5050 (4)	0.8101 (3)	3.1 (1)
C17	0.1540 (4)	0.5632 (4)	0.8774 (3)	3.8 (1)
C18	0.1756 (4)	0.5183 (4)	0.9493 (3)	3.7 (1)
C19	0.2373 (4)	0.4352 (4)	0.9301 (3)	3.2 (1)
C20	0.2979 (4)	0.3874 (4)	0.9940 (3)	3.1 (1)
C21	0.6351 (4)	0.1258 (4)	0.8909 (3)	3.3 (1)
C22	0.7551 (4)	0.1775 (5)	0.8878 (4)	4.6 (1)
C23	0.8540 (5)	0.1416 (6)	0.9301 (4)	5.8 (2)
C24	0.8353 (5)	0.0581 (5)	0.9759 (4)	6.1 (2)
C25	0.7155 (5)	0.0069 (5)	0.9770 (4)	5.2 (1)
C26	0.6154 (5)	0.0399 (4)	0.9339 (3)	3.9 (1)
C27	0.3561 (4)	0.2176 (4)	0.4628 (3)	3.5 (1)
C28	0.2463 (5)	0.1344 (4)	0.3930 (3)	4.2 (1)
C29	0.2406 (5)	0.1000 (5)	0.3006 (4)	5.0 (2)
C30	0.3437 (6)	0.1486 (5)	0.2791 (3)	5.5 (2)
C31	0.4523 (6)	0.2307 (7)	0.3463 (4)	7.5 (2)
C32	0.4581 (6)	0.2650 (6)	0.4391 (4)	6.3 (2)
C33	0.1686 (4)	0.6368 (4)	0.7144 (3)	3.2 (1)
C34	0.0457 (5)	0.6256 (5)	0.6652 (4)	5.2 (2)
C35	0.0123 (5)	0.7232 (5)	0.6576 (4)	5.3 (2)
C36	0.1010 (6)	0.8323 (4)	0.6994 (4)	5.3 (2)
C37	0.2269 (7)	0.8462 (4)	0.7459 (4)	6.1 (2)
C38	0.2594 (6)	0.7489 (5)	0.7530 (4)	4.8 (1)
C39	0.2787 (4)	0.4070 (4)	1.0872 (3)	3.2 (1)
C40	0.3440 (5)	0.5122 (5)	1.1591 (3)	5.5 (2)
C41	0.3226 (6)	0.5265 (6)	1.2425 (4)	6.5 (2)
C42	0.2389 (5)	0.4390 (5)	1.2554 (3)	5.4 (2)
C43	0.1742 (6)	0.3337 (6)	1.1857 (4)	6.2 (2)
C44	0.1958 (5)	0.3174 (5)	1.1015 (3)	4.8 (1)
C45	–0.0624 (5)	0.2624 (6)	0.7118 (4)	5.9 (2)
C46	–0.1732 (7)	0.255 (1)	0.6370 (7)	12.1 (3)
C47	–0.1554 (7)	0.2216 (9)	0.5493 (5)	9.9 (3)
C48	–0.0226 (6)	0.2384 (6)	0.5717 (4)	5.6 (2)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as $B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.

Figure 1 shows the structure of Zr(TPP)Cl_2(THF) (**1c**), which was obtained by recrystallization of Zr(TPP)Cl_2 from THF/dichloromethane/heptane. Selected bond distances and angles are given in Table III. The overall structure is similar to that of the previously known U(TPP)Cl_2(THF).[15] The coordination geometry about the zirconium may also be described as a 4:3

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(11) MolEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, The Netherlands, 1990.

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(14) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

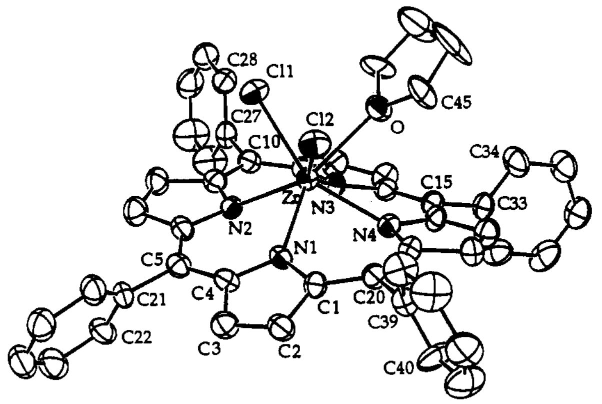

Figure 1. Structure of $Zr(TPP)Cl_2(THF)$ (**1c**) with atom labels (50% thermal ellipsoids).

Table III. Selected Bond Distances (Å) and Angles (deg) for **1c**

Zr–Cl1	2.473 (1)	Zr–N1	2.269 (3)
Zr–Cl2	2.499 (2)	Zr–N2	2.254 (4)
Zr–O	2.412 (3)	Zr–N3	2.272 (4)
		Zr–N4	2.251 (4)
Cl1–Zr–Cl2	83.64 (4)	O–Zr–N1	144.6 (1)
Cl1–Zr–O	75.99 (8)	O–Zr–N2	139.0 (1)
Cl1–Zr–N1	127.8 (1)	O–Zr–N3	74.7 (1)
Cl1–Zr–N2	77.21 (8)	O–Zr–N4	75.4 (1)
Cl1–Zr–N3	95.17 (8)	N1–Zr–N2	76.2 (1)
Cl1–Zr–N4	151.43 (9)	N1–Zr–N3	121.2 (1)
Cl2–Zr–O	80.29 (9)	N1–Zr–N4	77.8 (1)
Cl2–Zr–N1	77.6 (1)	N2–Zr–N3	77.4 (1)
Cl2–Zr–N2	126.6 (1)	N2–Zr–N4	126.5 (1)
Cl2–Zr–N3	154.5 (1)	N3–Zr–N4	77.6 (1)
Cl2–Zr–N4	91.3 (1)		

piano stool with the porphyrin occupying the square base. However, all the metal to ligand distances, Zr–Cl (2.473 (1) and 2.499 (2) Å), Zr–O (2.412 (3) Å), and Zr–N (2.251 (4)–2.272 (4) Å), are shorter than the corresponding values for $U(TPP)Cl_2(THF)$ (⟨U–Cl⟩ = 2.63 (1) Å; U–O = 2.50 (1) Å; ⟨U–N⟩ = 2.41 (1) Å), apparently due to the smaller ionic radius of Zr^{4+} (0.78 Å)[16] versus U^{4+} (0.95 Å).[16] The Zr atom is displaced 1.064 Å out of the mean 4-nitrogen plane and 1.252 Å out of the mean 24-atom porphyrin plane. As expected, the displacement of the metal atom out of the N_4 plane is smaller than that in $U(TPP)Cl_2(THF)$ (1.29 Å). The porphyrin ring is slightly domed and ruffled (see supplementary material), as in the uranium complex, but the deformation is not so severe as those in the sandwich complexes $Zr(TPP)_2$[17a,b] and $Zr(OEP)_2$.[17c]

In **1c**, one Zr–Cl bond is somewhat shorter than the other (2.473 (1) vs 2.499 (2) Å), but the origin of the difference is not clear. One may compare the structure of **1c** with those of $(COT)ZrCl_2(THF)$ (COT = η^8-cyclooctatetraenyl)[18] and Cp_2ZrCl_2.[19] The average Zr–Cl distance (2.486 (13) Å) and the Cl–Zr–Cl angle (83.64 (4)°) are comparable to those in $(COT)ZrCl_2(THF)$ (2.496 Å and 87.2 (1)°). However, the bond distance is longer and the angle is more acute than those in Cp_2ZrCl_2 (2.441 (5) Å and 97.2 (2)°), which may be attributed to the greater steric demand of the porphyrin ligand versus the Cp_2 moiety. Interestingly, the Zr–O bond distance (2.412 (3) Å) in **1c** is much longer than that in the COT complex (2.274 (2) Å). The rather long Zr–O bond distance suggests that the THF in **1c** is weakly bound to the metal, and this is consistent with the observation that the THF dissociates when **1c** is dissolved in $CDCl_3$, as evidenced by NMR spectroscopy. A long U–O bond distance (2.496 (9) Å) for the coordinated THF in $U(TPP)Cl_2(THF)$ has also been reported.[15]

The dichloride complexes can be converted to organometallic σ-complexes such as dialkyl or diaryl complexes by the reactions with alkyl- or aryllithium, as recently reported by Brand and Arnold.[5a] We have independently prepared the dimethyl complex $(TPP)ZrMe_2$ by treating **1b** with 2 equiv of LiMe in toluene. The product was characterized by spectroscopy and elemental analysis. In ^1H NMR spectrum the methyl protons appear as a singlet at −3.26 ppm due to strong shielding by the porphyrin ligand, which supports the formation of new Zr–Me bonds. Although there is no definite evidence, we believe that the dimethyl groups exist on the same side of the porphyrin plane since the cis geometry of the dialkyl groups in $Zr(OEP)(CH_2SiMe_3)_2$ has been confirmed by X-ray crystallography.[5a] The lower negative chemical shift value (−3.26 ppm) for the methyl protons compared to that for $(TPP)AlMe$[20] (−6.03 ppm) is consistent with the assumed cis geometry of the methyl groups: the methyl groups in $(TPP)ZrMe_2$ are not axially oriented as in (TPP)AlMe but rather at an angle with the normal to the porphyrin plane, which removes the H atoms of the methyl groups from the center of the shielding zone. The dimethyl complex is stable in the solid state but very sensitive to light, heat, and air/moisture in solution. In an early attempt to grow crystals of **2** for X-ray work, we obtained crystals of $(\mu\text{-}O)(\mu\text{-}OH)_2[Zr(TPP)]_2$[21] instead, which may be formed by the hydrolysis of **2**. The reaction chemistry of **2** is currently under investigation.

We also independently synthesized the organometallic π-complex $(\eta^5\text{-}1,2\text{-}C_2B_9H_{11})Zr(OEP)$, which was reported recently by Arnold et al.[5b] We obtained the complex from the reaction of $Zr(OEP)Cl_2$ with $Tl_2C_2B_9H_{11}$ (instead of the sodium salt as in ref 5b) in 64% yield. It has been fully characterized, and the structure has also been determined by X-ray crystallography. The spectroscopic properties and the structure are the same as the reported ones within experimental errors.[22] The compound is stable in the solid state but appears to be hydrolyzed slowly to form $[(\mu\text{-}OH)_3\{Zr(OEP)\}_2][1,2\text{-}C_2B_9H_{12}]$[21] in solution when it is exposed to air.

In summary, we have prepared $Zr(por)Cl_2$ (por = OEP, TPP) and determined the X-ray structure of $Zr(TPP)Cl_2(THF)$. We also have demonstrated that the dichloro complexes can be converted to novel organometallic complexes such as $Zr(TPP)Me_2$ and $Zr(OEP)(C_2B_9H_{11})$. We are currently studying the reactivity of the organometallic complexes.

Note Added in Proof. Synthesis and spectroscopic characterization of $Zr(TPP)Me_2$ appeared recently in the literature: Shibata, K.; Aida, T.; Inoue, S. *Chem. Lett.* **1992**, 1173–1176.

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Supplementary Material Available: Tables of crystallographic details, anisotropic thermal parameters, bond distances and angles, and dihedral angles between least-squares planes for $Zr(TPP)Cl_2(THF)$ (**1c**) and a diagram showing the displacements of atoms from the mean porphyrin planes of **1c** (9 pages). Ordering information is given on any current masthead page.

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(22) We observed the BH stretching band of **3** at 2547 cm^{-1} (in KBr pellet) instead of 2514 cm^{-1} (in Nujol mull) as reported.[5b] This difference may be ascribed to the medium effect, but the sample used in ref 5b may have been hydrolyzed during the sample preparation, as we observed the BH peak at 2514 cm^{-1} for $[(\mu\text{-}OH)_3\{Zr(OEP)\}_2][1,2\text{-}C_2B_9H_{12}]$.[21]