Organometallics **1993**, *12*, 3655–3665

Early Transition Metal Porphyrins: Synthesis, Characterization, and Reactivity of Novel Out-of-Plane Cis-Ligated Zirconium Porphyrin Derivatives

Holger Brand and John Arnold*

Department of Chemistry, University of California, Berkeley, California 94720

Received June 23, 1993[⊗]

A new class of coordinatively unsaturated zirconium porphyrin compounds, $(OEP)ZrR_2$ [OEP = dianion of octaethylporphyrin; R = chloride, trifluoromethanesulfonate (triflate, OTf), acetate, alkoxide, alkyl, aryl; R_2 = cyclooctatetraenyl], has been prepared. $(OEP)ZrCl_2$, prepared by metathesis between $Li_2OEP(DME)_n$ and $ZrCl_4(DME)$, serves as starting material for further functionalization. The organometallic derivatives are very reactive, readily undergoing protonolysis, hydrogenolysis, and insertion of CO_2 and acetone into the Zr–C bonds. Cis-ligation in these out-of-plane zirconium porphyrin compounds has been inferred from ^1H NMR measurements and confirmed in three derivatives by X-ray diffraction. Crystallographic data are as follows. $(OEP)ZrCl_2{\cdot}0.5Tol$: space group $P\bar{1}$ with $a = 9.870(2)$ Å, $b = 14.143(3)$ Å, $c = 14.498(3)$ Å, $\alpha = 66.257(17)°$, $\beta = 88.003(17)°$, $\gamma = 79.645(17)°$, $V = 1820.9(8)$ Å^3, and $Z = 2$. $(OEP)Zr(O^tBu)_2$: space group $P\bar{1}$ with $a = 12.4441(12)$ Å, $b = 13.1594(21)$ Å, $c = 13.9541(18)$ Å, $\alpha = 89.972(11)°$, $\beta = 99.192(9)°$, $\gamma = 115.487(11)°$, $V = 2045.7(10)$ Å^3, and $Z = 2$. $(OEP)ZrMe_2$: space group $P\bar{1}$ with $a = 10.007(3)$ Å, $b = 13.062(4)$ Å, $c = 14.558(3)$ Å, $\alpha = 82.83(2)°$, $\beta = 88.24(2)°$, $\gamma = 79.98(2)°$, $V = 1859.1(12)$ Å^3, and $Z = 2$.

Introduction

Many important stoichiometric and catalytic transformations mediated by d^0 transition metals entail ligation of these metals by two cyclopentadienyl groups.[1] Reactions promoted by these metallocene derivatives involve fundamental processes such as insertion of small molecules into metal alkyl or hydride bonds,[2] cyclization of small molecules,[3] and metathesis of σ-bonds.[4] Efforts to alter the ligand environment has centered around bulky alkoxides[5] or amides[6] and chelating ligands such as Schiff bases[7] or tetraaza[14]annulenes.[8] We are interested in exploring early metal porphyrin derivatives of the heavier second and third row elements were the metal lies out of the porphyrin plane as a result of its large radius, thus constraining additional ligands on the metal to be cis.[9] For zirconium, few derivatives are known apart from oxo-ligated derivatives originally developed by Buchler and co-workers.[10,11] The vast majority of known metalloporphyrin chemistry is based on derivatives involving late transition metals, where an in-plane geometry directs ligands to mutually trans positions.[12] Due to the lack of readily accessible cis coordination sites, mechanisms involving free radicals dominate reactivities of the latter group of compounds.[13]

In this paper we report (i) a general synthetic route to novel out-of-plane cis-ligated zirconium porphyrin derivatives based on the metathesis reaction between a porphyrin dianion[14] and zirconium halides, (ii) a detailed structural study of a range of $(OEP)ZrX_2$ derivatives and

---

[⊗] Abstract published in *Advance ACS Abstracts*, August 15, 1993.

[1] Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and Organo-Hafnium Compounds*; John Wiley: New York, 1986.

[2] (a) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (c) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

[3] (a) Erker, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (c) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65.

[4] (a) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177. (b) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (c) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846. (d) McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966. (e) Bulls, A. R.; Bercaw, J. E.; Manriquez, J. M.; Thompson, M. E. *Polyhedron* **1988**, *7*, 1409.

[5] (a) Lubben, T. V.; Wolczanski, P. T.; Van Dyne, G. D. *Organometallics* **1984**, *3*, 977. (b) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 424.

[6] (a) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 1724. (b) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 2928. (c) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (d) Cummins, C. C.; Schaller, C. P.; Van Dyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffman, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985.

[7] Floriani, C. *Polyhedron* **1989**, *8*, 1717.

[8] (a) Cotton, F. A.; Czuchajowska, J. *Polyhedron* **1990**, *9*, 2553. (b) De Angelis, S.; Solari, E.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 2520 and references therein. (c) Yang, C.-H.; Ladd, J. A.; Goedken, V. L. *J. Coord. Chem.* **1988**, *18*, 317 and references therein.

[9] (a) Brand, H.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 2266. (b) Arnold, J.; Hoffman, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 8620. (c) Arnold, J.; Johnson, S. E.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 3996. (d) Arnold, J.; Hoffman, C. G.; Dawson, D. Y. *Organometallics*, in press.

[10] (a) Buchler, J. W.; Eikelmann, G.; Puppe, L.; Rohbock, K.; Schneehage, H. H.; Weck, D. *Liebigs Ann. Chem.* **1971**, *745*, 135. (b) Buchler, J. W.; Schneehage, H. H. *Z. Naturforsch. B* **1973**, *28*, 433. (c) Gouterman, M.; Karle-Hanson, L.; Khalil, G.-E.; Buchler, J. W.; Rohbock, K.; Dolphin, D. *J. Am. Chem. Soc.* **1975**, *97*, 3142. (d) Buchler, J. W.; Folz, M.; Habets, H.; van Kaam, J.; Rohbock, K. *Chem. Ber.* **1976**, *109*, 1477. (e) Buchler, J. W.; De Cian, A.; Fischer, J.; Hammerschmitt, P.; Weiss, R. *Chem. Ber.* **1991**, *124*, 1051.

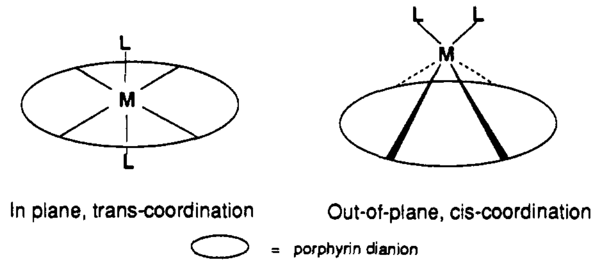
[11] For other recent accounts of zirconium porphyrins see: (a) Berezin, B. D.; Lomova, T. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1981**, *26*, 203. (b) Kim, K.; Lee, W. S.; Kim, H.-J.; Cho, S.-H.; Girolami, G. S.; Gorlin, P. A.; Suslick, K. S. *Inorg. Chem.* **1991**, *30*, 2652. (c) Shibata, K.; Aida, T.; Inoue, S. *Tetrahedron Lett.* **1992**, *33*, 1077. (d) Shibata, K.; Aida, T.; Inoue, S. *Chem. Lett.* **1992**, 1173. (e) Kim, H.-J.; Whang, D.; Kim, K.; Do, Y. *Inorg. Chem.* **1993**, *32*, 360.

[12] (a) Smith, K. M. *Porphyrins and Metalloporphyrins*; Elsevier: New York, 1975. (b) Dolphin, D. *The Porphyrins*; Academic Press: New York, 1978; Vols. 1–4. (c) Guilard, R.; Lecomte, C.; Kadish, K. M. *Struct. Bonding* **1968**, *64*, 207. (d) Guilard, R.; Kadish, K. M. *Chem. Rev.* **1988**, *88*, 1121.

[13] (a) Brothers, P. J.; Collman, J. P. *Acc. Chem. Res.* **1986**, *19*, 209. (b) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305. (c) Wayland, B. B.; Ba, S.; Sherry, A. E. *Inorg. Chem.* **1992**, *31*, 148.

[14] (a) Arnold, J. *J. Chem. Soc., Chem. Commun.* **1990**, 976. (b) Arnold, J.; Dawson, D. Y.; Hoffman, C. C. *J. Am. Chem. Soc.* **1993**, *115*, 2707.

0276-7333/93/2312-3655$04.00/0



a comparison to related metallocenes, and (iii) an investigation of the reactivity of *cis*-dialkyl metalloporphyrins toward small molecules. In particular, we are pursuing the question of how the relatively hard ligand environment exerted by the porphyrin ligation combined with the steric demand of this large ligand[15] influences its reactivity in comparison to analogous zirconocene compounds. A preliminary account of part of this work has appeared.[9a]

Results and Discussion

Synthesis of (OEP)Zr Derivatives. A useful starting material for the synthesis of a variety of derivatives of zirconium octaethylporphyrin compounds is the corresponding dichloride (OEP)ZrCl$_2$. Initially, we obtained (OEP)ZrCl$_2$ by reaction of (THF)$_4$Li$_2$(OEP) with 1.2 equiv of ZrCl$_4$(THT)$_2$ (THT = tetrahydrothiophene) in refluxing DME (eq 1).

$$\mathrm{Li_2(THF)_4OEP + ZrCl_4(THT)_2 \xrightarrow[\text{DME}]{} \underset{60\%}{(OEP)ZrCl_2{\cdot}0.5Tol} + \underset{25\%}{(OEP)_2Zr}} \quad (1)$$

Dark red, air-stable crystals of the hemi-toluene solvate of (OEP)ZrCl$_2$ were obtained in 60% yield after Soxhlet extraction with toluene. However, separation of the supernatant afforded a second product, which was identified as (OEP)$_2$Zr[10e,11b] (by ^{1}H NMR and UV/vis spectroscopy) in about 25% yield (relative to OEP). Subsequently, we found that if the reaction is performed in CH$_2$Cl$_2$ at room temperature, virtually none of the sandwich compound is generated (eq 2).

$$\mathrm{Li_2(DME)_{\mathit{n}}OEP + ZrCl_4(DME) \xrightarrow[\text{CH}_2\text{Cl}_2]{} \underset{80\%}{(OEP)ZrCl_2{\cdot}0.5Tol}} \quad (2)$$

As monitored by ^{1}H NMR spectroscopy in CD$_2$Cl$_2$, the reaction was complete within 10 min and no byproducts were detected. After extraction of excess Zr salts with DME, the crude product was Soxhlet extracted to afford (OEP)ZrCl$_2$ in 80% yield on scales up to 5 g. The dichloride is insoluble in hexane and diethyl ether, moderately soluble in THF and toluene, and very soluble in methylene chloride and chloroform. As expected for an out-of-plane structure the diastereotopic methylene protons[16] of the OEP ligand give rise to a complicated multiplet in the ^{1}H NMR spectrum (Figure 1). The compound sublimes without decomposition, and a strong parent ion is seen in the EI mass spectrum. Solvent free (OEP)ZrCl$_2$ can be obtained by heating a sample to 100 °C at 10^{-3} Torr for 24 h. Addition of 1 equiv of pyridine to a CDCl$_3$ solution of (OEP)ZrCl$_2$ results in broad upfield shifted signals for the exchanging pyridine in the ^{1}H NMR spectrum. Exchange takes place at temperatures as low at −40 °C. The pyridine signals however sharpen upon further cooling to −50 °C. Considering the electron deficient nature of (OEP)ZrCl$_2$, we attribute the weak binding of pyridine to steric congestion around the zirconium. A similar argument was presented to explain the rather long Zr–O bond length in the related (TPP)ZrCl$_2$(THF), which was found to dissociate THF in solution at room temperature.[11e]

Treating (OEP)ZrCl$_2$ with an excess of Me$_3$SiOTf in toluene generates (OEP)Zr(OTf)$_2$ which was isolated as red crystals in 71% yield (Scheme I).

The ^{1}H NMR spectrum of (OEP)Zr(OTf)$_2$ in CDCl$_3$ indicates the presence of two species, the ratio of the two, as determined by integration of the signals corresponding to the meso-hydrogens at δ 10.65 (fwhh = 5.1 Hz) and 10.12 (fwhh = 6.7 Hz) (room temperature), is 8:7.5 at −85 °C, 8:4 at room temperature, and 8:3.5 at 50 °C (fwhh = 13.5 and 22 Hz). Two signals with relative intensities of 3:1 are visible in the ^{19}F NMR spectrum at room temperature in CDCl$_3$. We believe the two species observed in CDCl$_3$ are (OEP)Zr(OTf)$_2$ and [(OEP)Zr(OTF)]$^+$[OTf]$^-$, with the lower intensity signal assigned to the free triflate in the latter. In more polar solvents such as CD$_3$CN, however, only one species with sharp features in the ^{1}H NMR spectrum and one ^{19}F NMR resonance (δ 11.79) was observed. In addition, conductivity measurements indicate that (OEP)Zr(OTf)$_2$ is a 2:1 electrolyte in CH$_3$CN, implying the presence of a (OEP)Zr dication, probably coordinated by two or more solvent molecules, with two triflate counteranions. Since the methylene hydrogens of the dication are diastereotopic, we assume that the zirconium is still displaced out of the porphyrin plane. In the related zirconocene compound Cp$_2$Zr(OTf)$_2$THF, weak donors are known to displace both OTf$^-$ ligands to form dicationic species.[17]

Reaction of (OEP)ZrCl$_2$ with an excess of NaOAc in acetic acid afforded the known diacetate (OEP)Zr(OAc)$_2$ after crystallization from acetic acid/water in 95% yield. The structure of this compound has been briefly mentioned and shows the metal to be eight-coordinate with bidentate, cis acetate ligands.[18] (OEP)Zr(OAc)$_2$ can be converted to (OEP)Zr(OAc)Cl by heating a toluene suspension of (OEP)Zr(OAc)$_2$ with an excess of Me$_3$SiCl at reflux. Using the more potent chloride transfer reagent SiCl$_4$, the dichloride is regenerated in quantitative yield. This allows for an easy way to recuperate precious (OEP)ZrCl$_2$, as the diacetate is easily and almost quantitatively generated from all the porphyrin derivatives discussed here with the exception of (OEP)$_2$Zr.

Alkoxide derivatives were prepared easily and in good yields by metathesis between (OEP)ZrCl$_2$ and the appropriate alkali metal alkoxides. For example (OEP)Zr(OSiMe$_3$)$_2$ and (OEP)Zr(O^{t}Bu)$_2$ were obtained from (OEP)ZrCl$_2$ and 2 equiv of KOSiMe$_3$ and LiO^{t}Bu, respectively, in 65% and 70% yield. The compounds are moisture-sensitive but are otherwise stable to heat and light. The mixed alkoxide/chloride derivative (OEP)Zr(O^{t}Bu)Cl was prepared from (OEP)ZrCl$_2$ and 1 equiv of

---

[15] On the basis of our X-ray data, the cone angle of the OEP ligand in (OEP)ZrMe$_2$ is estimated to be approximately 168°.

[16] Busby, C. A.; Dolphin, D. *J. Magn. Reson.* **1976**, *23*, 211.

[17] Thewaldt, U.; Lasser, W. *Z. Naturforsch. B* **1983**, *38*, 1501.

[18] Hoard, J. L. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: New York, 1975; p 347.

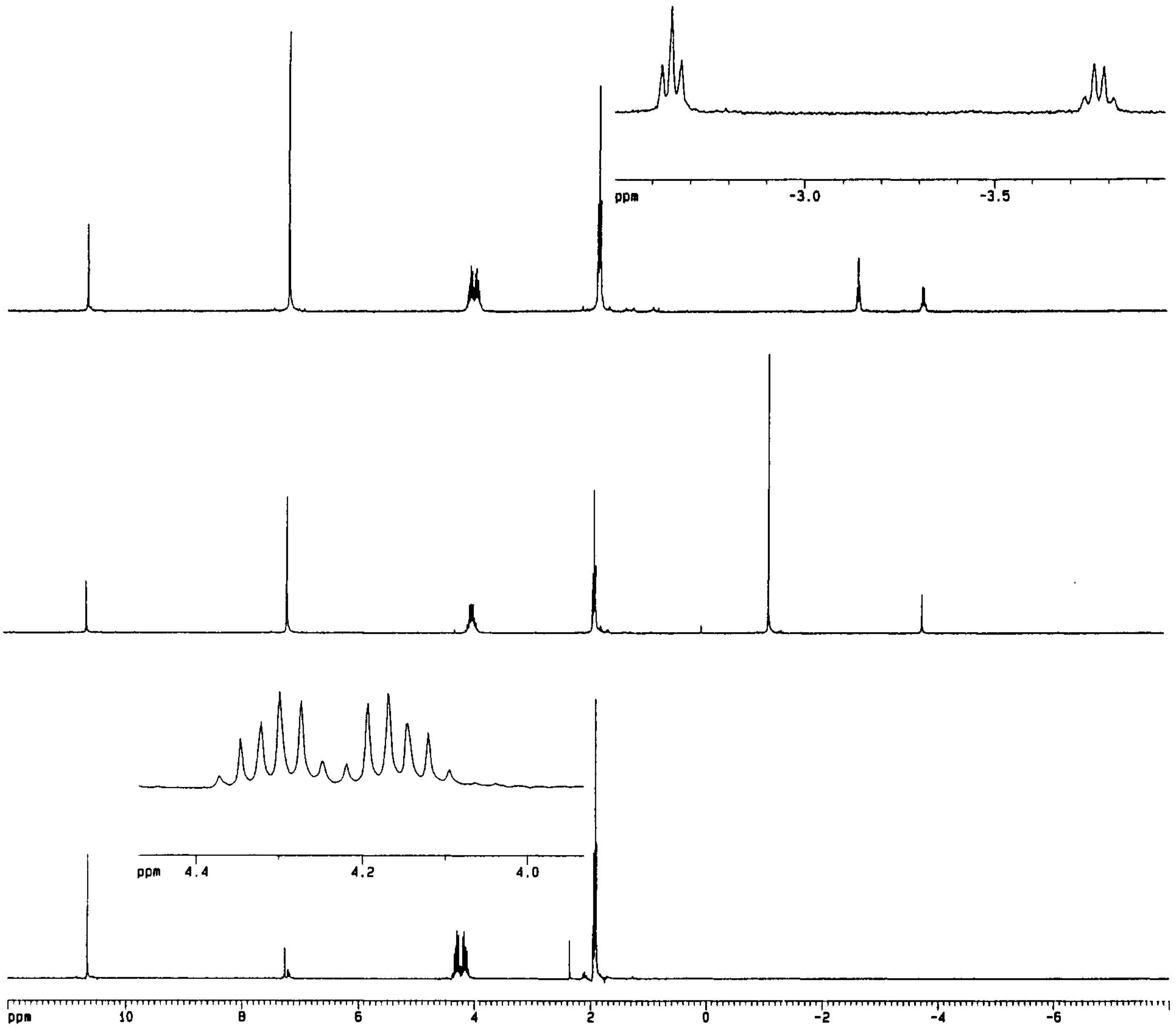


Figure 1. 400-MHz ^{1}H NMR spectra of (OEP)$ZrCl_2$·0.5Tol (bottom, $CDCl_3$), (OEP)Zr(CH_2SiMe_3) (middle, benzene-d_6), and (OEP)$ZrEt_2$ (top, benzene-d_6).

LiO^{t}Bu in CH_2Cl_2 at low temperature and was isolated in 95% yield. We were unable, however, to prepare a methoxide derivative either from (OEP)$ZrCl_2$ and 2 equiv of LiOMe or from (OEP)$ZrMe_2$ and methanol. Several attempts to prepare (OEP)Zr amides also remained fruitless.

(OEP)$ZrCl_2$ is readily converted into a variety of organometallic derivatives using straightforward metathetical routes, as shown in Scheme II.

(OEP)Zr(CH_2SiMe_3)$_2$ and (OEP)Zr(p-$C_6H_4{}^tBu$)$_2$ were prepared in quantitative yield from (OEP)$ZrCl_2$ and 2 equiv of organolithium reagent. The choice of solvent is crucial and, in general, strongly coordinating solvents such as THF, DME, or pyridine interfere with these reactions. In these cases a myriad of products is obtained and both UV/vis and ^{1}H NMR spectra indicate that the symmetry of the porphyrin ring has been reduced. We suspect that alkylation of the porphyrin moiety has taken place in these cases.[19] Alkylation of a macrocyclic ligand has been reported during alkylation of the related [tetramethyltetraazadibenzo[14]annulenato]zirconium dichloride.[20] (OEP)Zr(p-$C_6H_4{}^tBu$)$_2$ could not be isolated in pure form, since it slowly decomposes at room temperature to unidentifiable products. As expected, the ^{1}H NMR signals for the aryl ring are shifted to a high field. The ortho- and meta-protons resonate at δ 3.44 and 5.83 ppm, respectively, and the butyl protons appear at 0.61 ppm.[21] Reactions of (OEP)$ZrCl_2$ with MeLi or EtLi did not yield the expected dialkylated derivatives. However, (OEP)$ZrMe_2$ and (OEP)$ZrEt_2$ were prepared cleanly and in good yields using organomagnesium reagents. Conversion of (OEP)$ZrCl_2$ to (OEP)$ZrMe_2$ was slow in toluene; however, in CH_2Cl_2 (even at low temperature) the alkylation is very fast, presumably due to the much greater solubility of (OEP)$ZrCl_2$ in CH_2Cl_2 than in toluene. Although (OEP)$ZrEt_2$ is thermally much more stable than the corresponding zirconocene diethyl, it slowly generates ethylene (>0.35 equiv) and ethane (>0.48 equiv), when heated to 50 °C, as judged by ^{1}H NMR spectroscopy. Addition of excess 1-hexene to (OEP)$ZrEt_2$ in benzene-d_6 does not generate any zirconium hexyl species or hexane, thus indicating that β-hydrogen elimination is not necessarily responsible for the decomposition of (OEP)$ZrEt_2$.

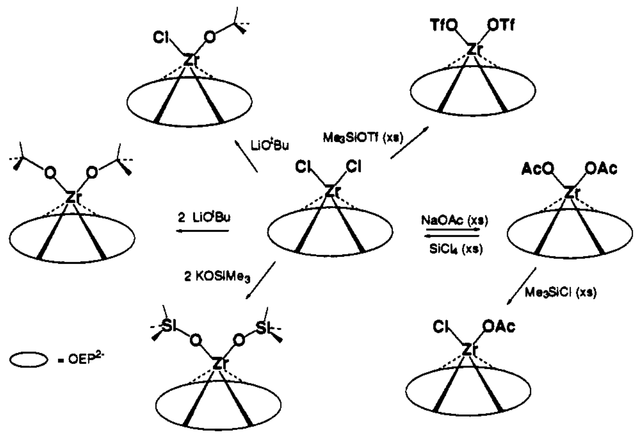
---

[19] It is well-known that strongly coordinating solvents promote single electron transfer reactions of organolithium reagents, thus providing a pathway for ring alkylation. See: Wakefield, B. J. *Organolithium Methods*; Academic Press: New York, 1988.

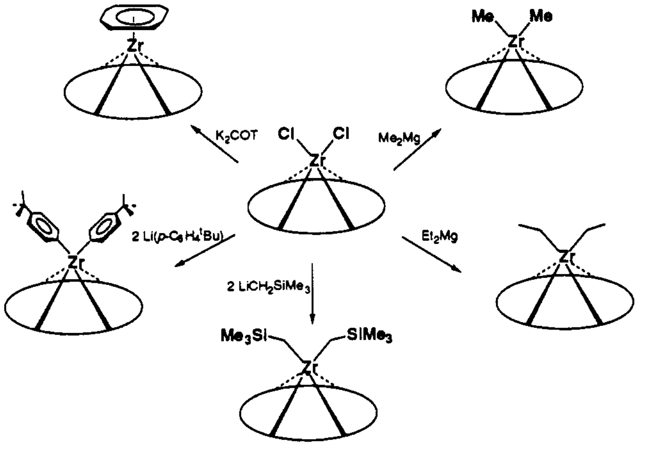
[20] Floriani, C.; Ciurli, S.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 70.

[21] The higher upfield shifts seen in *trans*-diphenyl species such as (OEP)$RuPh_2$ presumably result from the closer proximity of the phenyl ligands to the porphyrin. See for example: Shista, C.; Ke, M.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1986**, 787.

Scheme I



Scheme II



The porphyrin methylene hydrogens in all of the derivatives discussed above display a complicated multiplet rather than a quartet in the ^{1}H NMR spectrum. This is an indication for the out-of-plane nature of these compounds and implies cis coordination geometry for additional ligands. This has been confirmed for all derivatives studied by X-ray crystallography (see below). In general, the anisotropy of the aromatic porphyrin macrocycle induces large upfield shifts in the ^{1}H NMR spectrum and causes the α-, β-, and γ-protons of the attendant alkyl groups to be well separated (usually by more than 1 ppm, see Figure 1) and, therefore, easily assigned.[22]

In related (OEP)Sc derivatives, we have shown that complexation of many-electron π-ligands such as η^5-Cp, Cp*, and indenyl, is readily accomplished by virtue of the out-of-plane, electron-deficient nature of the (OEP)Sc fragment.[9b] For zirconium the related cyclooctatetraene (COT) derivative was also prepared. Treatment of (OEP)ZrCl$_2$ with K$_2$COT in THF gave a dark red solution from which the air-sensitive 18-electron compound (OEP)Zr(C$_8$H$_8$) was isolated as red needles in 20% yield. We did not see evidence for the onset of any coalescence phenomena when a sample of (OEP)Zr(C$_8$H$_8$) in CD$_2$Cl$_2$ was cooled to −80 °C. This does not necessarily infer a planar η^8-COT ligand, as the related species (COT)$_2$Zr also does not exhibit fluxionality in its ^{1}H NMR spectra, yet it is known to coordinate one ring η^4, as shown by X-ray crystallography.[23] In an earlier report, the preparation and structure of the related carborane complex, (OEP)Zr(η^5-C$_2$B$_9$H$_{11}$), was described.[9c]

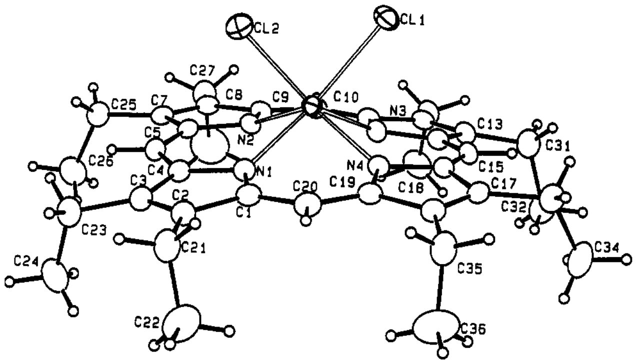


Figure 2. Molecular structure of (OEP)ZrCl$_2$. Thermal ellipsoids are scaled to represent the 50% probability level.

Table I. Selected Metrical Parameters for (OEP)ZrCl$_2$·0.5Tol

bond length, Å		bond angle, deg	
Zr–Cl1	2.473(1)	Cl1–Zr–Cl2	81.70(3)
Zr–Cl2	2.459(1)	N1–Zr–N3	127.32(10)
Zr–N1	2.232(3)	N2–Zr–N4	133.77(10)
Zr–N2	2.213(3)		
Zr–N3	2.235(3)		
Zr–N4	2.206(3)		

All the organometallic (OEP)Zr compounds are extremely sensitive to moisture, oxygen, and prolonged ambient room lighting. This high reactivity, combined with the fact that the hydrolysis products have similar solubility properties (see below) makes isolation of these derivatives in pure form synthetically challenging.

X-ray Structure Determinations. We begin with descriptions of the general structural features of each molecule, followed by a comparison of these (OEP)ZrX$_2$ compounds with analogous Cp$_2$ZrX$_2$ derivatives (Figure 5). The structure of (OEP)Zr(CH$_2$SiMe$_3$)$_2$ was described in our preliminary account and is briefly summarized in the latter section.

(OEP)ZrCl$_2$ (Table I). The structure consists of two molecules of the compound packed into the cell with one molecule of toluene per unit cell. There are no exceptionally short contacts in the cell, but the packing is efficient. As seen in Figure 2, the chlorides are cis to one another with the ZrCl$_2$ unit located well above the N$_4$ plane (0.93 Å). The porphyrin is domed and also slightly ruffled, as can be seen by the variation of the angles between the least-squares plane of the porphyrin and the individual pyrrole rings (see supplementary material). The bond distances and angles in the porphyrin are unremarkable. The variation in the Zr–N bond length can be traced to the ruffling of the porphyrin ring. The nitrogens on the more coplanar porphyrins are just a little further from the Zr. The orientation of the ZrCl$_2$ plane seems to be controlled by packing forces rather than internal contacts. Both Zr–Cl bonds are shorter than those in the recently determined structure of (TPP)ZrCl$_2$(THF), which shows Zr–Cl bond lengths of 2.473(1) and 2.499(2) Å. Interest-

---

[22] Similar or larger upfield shifts have been observed in metalloporphyrins having alkyl groups in mutual trans positions. See for example: (a) Balch, A. L.; Cornman, C. R.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 2963. (b) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E. *J. Am. Chem. Soc.* **1985**, *107*, 6110. (c) Cloutour, C.; Lafargue, D.; Richards, J. A.; Pommier, J.-C. *J. Organomet. Chem.* **1977**, *137*, 157. (d) Maskasky, J. E.; Kenney, M. E. *J. Am. Chem. Soc.* **1973**, *95*, 1443.

[23] Rogers, D. M.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1991**, *10*, 2419.

Table II. Selected Metrical Parameters for (OEP)Zr(O^{t}Bu)$_2$

bond length, Å		bond angle, deg	
Zr–O1	1.947(2)	O1–Zr–O2	90.08(9)
Zr–O2	1.948(2)	Zr–O1–C37	175.61(20)
C37–O1	1.414(4)	Zr–O2–C41	178.10(20)
C41–O2	1.420(4)	N1–Zr–N3	126.36(9)
Zr–N1	2.284(2)	N2–Zr–N4	123.61(9)
Zr–N2	2.295(2)		
Zr–N3	2.287(2)		
Zr–N4	2.307(2)		

ingly, the Cl–Zr–Cl angle in the latter is *less* acute (83.64°) than in the base free (and presumably less hindered) (OEP)ZrCl$_2$ (81.7°).

(OEP)Zr(O^{t}Bu)$_2$ (Table II). The structure consists of molecules of the compound packed in the unit cell with no exceptionally close contacts between them. The structure of the molecule (Figure 3) shows the two O^{t}Bu ligands cis to each other, as expected on the basis of spectroscopic data. The plane of O1, O2, and Zr approximately bisects two of the N–Zr–N angles, and the coordination of Zr is approximately trigonal prismatic with the Zr 1.06 Å out of plane. One of the methyl carbons (C32) is disordered in an apparently 50:50 ratio between "up" and "down". Inspection of the packing shows that it has about the same number of intermolecular contacts in each position. The porphyrin has the usual amount of dome shape associated with this type of coordination. The O^{t}Bu ligands are coordinated in a linear fashion, which may be taken as evidence for strong O–Zr π-bonding. We also note, however, that the porphyrin is bent around the C10–C20 axis, and it appears that this bending is due to steric interactions of the O^{t}Bu ligands, with close contacts C6–C39 and C14–C43 in the range of 3.4 Å and the contact between C38 and C42 being 3.7 Å to "lock" the configuration. The larger out-of-plane displacement of the zirconium by more than 0.1 Å in comparison to the other structures discussed here can also be traced back to the steric interactions of the bulky alkoxides with the porphyrin moiety. Otherwise the pyrrole rings are planar and the delocalization appears normal.

(OEP)ZrMe$_2$ (Table III). The crystal structure consists of two molecules of (OEP)ZrMe$_2$ packed into the unit cell with molecules of dichloromethane loosely held in holes between the molecules (see Figure 4). The molecules form double layers, with the ethyl groups making contacts between the layers. The dichloromethane has large thermal parameters and is clearly only loosely held in its hole. The porphyrin is domed with only a small amount of ripple, and the Zr atom is 0.89 Å out of plane. The angles of the pyrrole planes to the N$_4$ plane are 11.2, 4.2, 8.1, and 4.5°. The C–Zr–C plane is twisted 37° from the N1–Zr–N3 plane and 55° from the N2–Zr–N4 plane. All distances and angles in the porphyrin appear normal. The structure is closely related to the (trimethylsilyl)methyl derivative reported earlier, as shown in Figure 5. The Zr–C bonds in the dimethyl are significantly longer than those in the latter complex, in contrast to the metallocene cases where Zr–C bond lengths in the two derivatives are essentially equivalent. At present we cannot provide a reasonable explanation for these findings, although we can rule out the presence of chloride contaminants that would artificially "lengthen" the bond,[24] since the batch used for crystallography was pure dimethyl by ^{1}H NMR spectroscopy. The C–Zr–C angle is more acute in the dimethyl, presumably reflecting the lower steric bulk of the methyl groups relative to the CH$_2$SiMe$_3$ ligands.

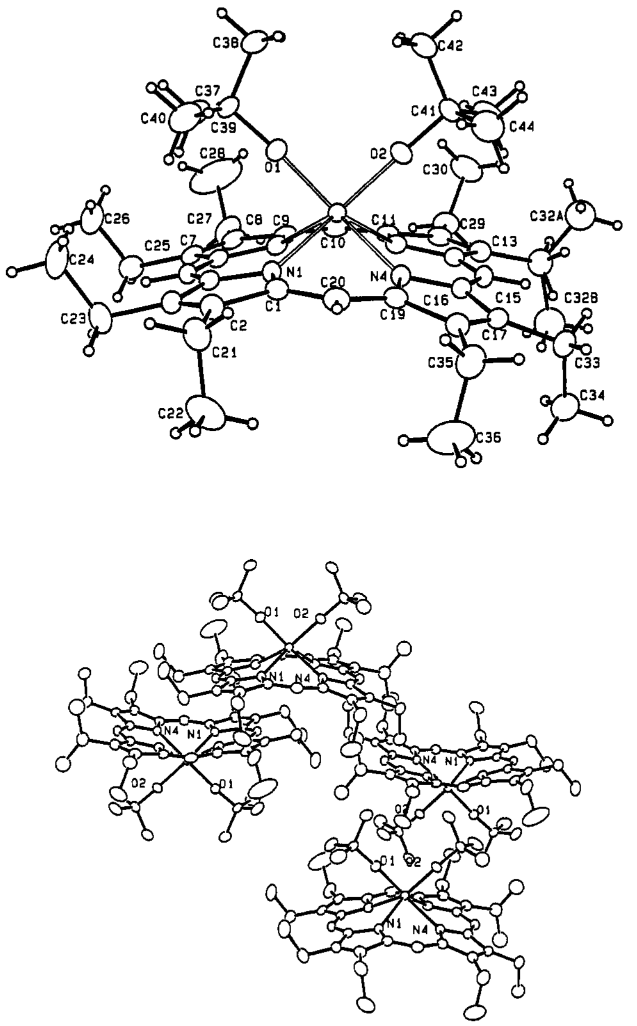


Figure 3. Side view of the molecular structure of (OEP)Zr(O^{t}Bu)$_2$ (top) and crystal packing diagram (bottom). Thermal ellipsoids are scaled to represent the 50% probability level.

Table III. Selected Metrical Parameters for (OEP)ZrMe$_2$·CH$_2$Cl$_2$

Bond Length, Å		Bond Angle, deg	
Zr–C37	2.352(4)	C37–Zr–C38	78.21(12)
Zr–C38	2.334(4)	N1–Zr–N3	131.68(10)
Zr–N1	2.242(3)	N2–Zr–N4	133.91(10)
Zr–N2	2.225(3)		
Zr–N3	2.236(3)		
Zr–N4	2.221(3)		

Comparison of Related (OEP)ZrX$_2$ and Cp$_2$ZrX$_2$ Structures. Figure 5 shows a comparison of some of the more important metrical parameters for related compounds. (Although we were unable to find any structural determinations for simple zirconocene bis(alkoxides), Stephan has described the structure of a related bridging bis(alkoxide), Cp$_2$Zr(OCH$_2$CMe$_2$CH$_2$O)ZrCp$_2$, which is given for comparison.)[25d] From these data, we note the following trends: (i) In general, the Zr–X bond length is marginally shorter in Cp$_2$Zr derivatives[25] in all cases except the alkoxide where the Zr–O bonds are equivalent within experimental error. (ii) For all four porphyrin structures, the X–Zr–X bond angle is considerably more acute (by

---

[24] Yoon, K.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 2210.

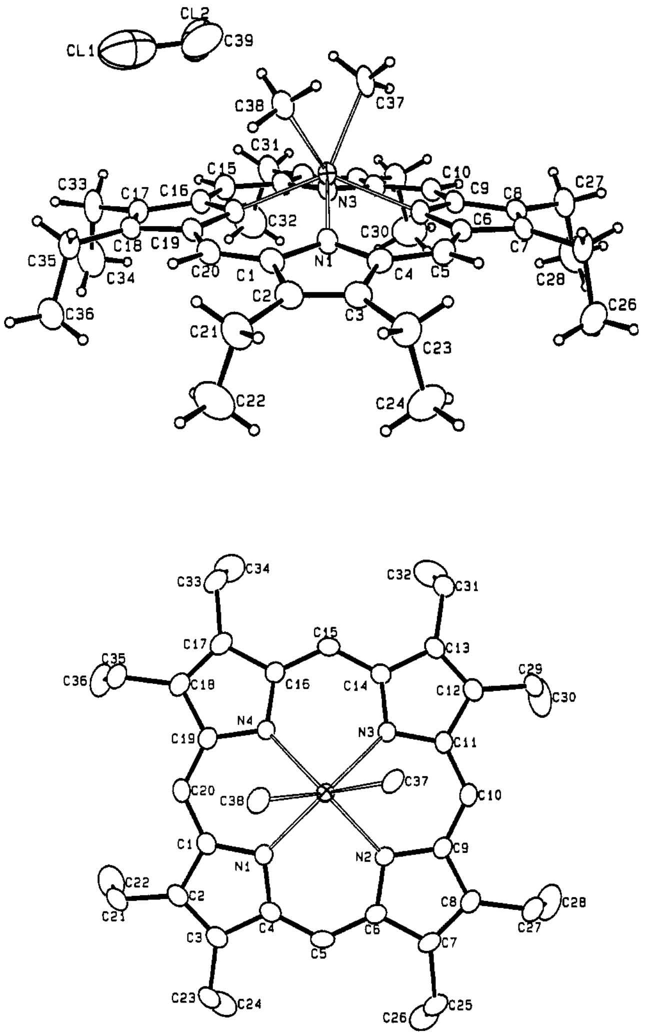


Figure 4. Side view of the molecular structure of (OEP)ZrMe$_2$ showing the disordered CH$_2$Cl$_2$ (top) and top view (bottom). Thermal ellipsoids are scaled to represent the 50% probability level.

11–17°) than that in the d^0 zirconocene analogues. This is no doubt due to the increased steric demand of the porphyrin as compared to two cyclopentadienyl ligands in these d^0 systems. Similar data have been described for group 4 Schiff base and tetraaza[4]annulene compounds.[20,26,27] Note, however, that with population of the metallocene a$_1$ orbital to form related d^1 compounds such as Cp$_2$Nb(SPh)$_2$[28] or [Cp$_2$MoCl$_2$]$^+$,[25a] the corresponding angles may be much more acute (S–Nb–S = 74.8(1)°; Cl–Mo–Cl = 82.0(2)°), showing that steric factors *alone* need not necessarily control X–M–X interactions.

Reactivity Studies. Protonolysis. Careful addition of 1 equiv of H$_2$O to (OEP)Zr(CH$_2$SiMe$_3$)$_2$ in CDCl$_3$ generates 2 equiv of SiMe$_4$ and a new porphyrin compound **A**, in which the meso-protons are shifted upfield to δ 9.40 in the ^{1}H NMR spectrum. Addition of 1.5 equiv of H$_2$O produces a different porphyrin species **B** with a corresponding shift at δ 9.60 along with a new peak at −7.56 (ratio 2:1). We assign **A** and **B** the structures shown in Scheme III on the following basis: meso-protons generally resonate in the narrow range δ 10.0–10.7 in diamagnetic, monomeric OEP complexes,[29] whereas a range of δ 9.5–9.7 is found for μ-oxo or μ-hydroxo OEP dimers.[9d,10b,30] The signal at −7.56 is assigned to the bridging O*H* groups with precedents for such high-field shifted resonances in other μ-hydroxo OEP dimers.[9d,30c]

In an attempt to isolate this compound, a pyridine solution of (OEP)Zr(CH$_2$SiMe$_3$)$_2$ was allowed to slowly evaporate in air, resulting in the formation of small crystals

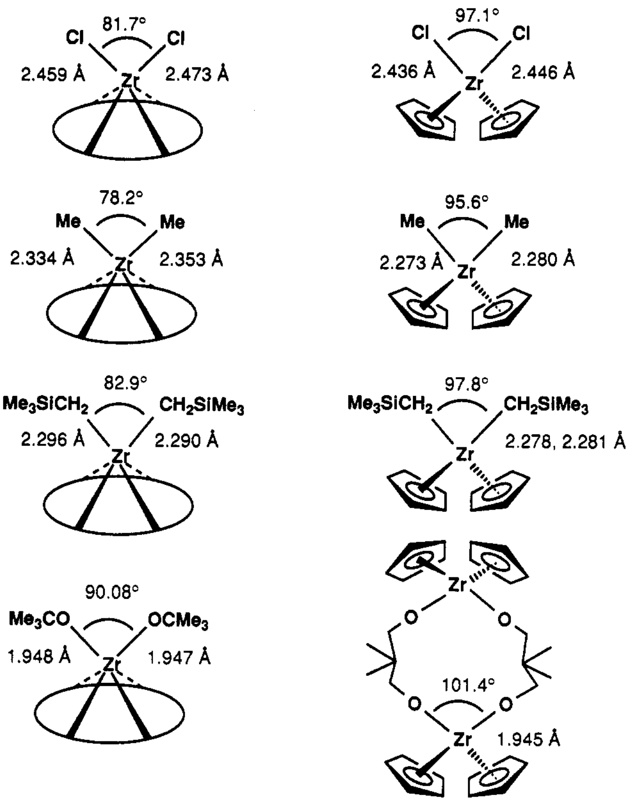
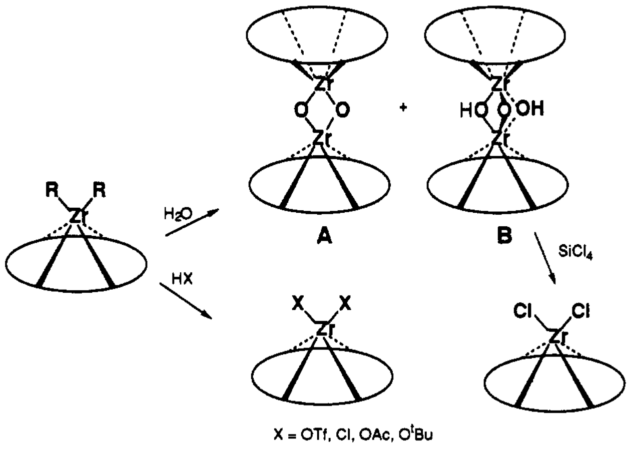


Figure 5. Comparison of bond angles and lengths of (OEP)Zr vs Cp$_2$Zr compounds.

Scheme III



---

(25) (a) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Ress, G. V. *Acta Crystallogr.* **1974**, *B30*, 2290. (b) Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Pentilla, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750. (c) Jeffery, J.; Lappert, M. F.; Luong-Thi, N. T.; Webb, M.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1593. (d) Stephan, D. W. *Organometallics* **1990**, *9*, 1718.

(26) De Angelis, S.; Solari, E.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 2520.

(27) Corazza, F.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1990**, 1335.

(28) Darensbourg, M. Y.; Silva, R.; Reibenspies, J.; Prout, C. K. *Organometallics* **1989**, *8*, 1315.

(29) Scheer, H.; Katz, J. J. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: New York, 1975; p 399.

(30) (a) Lecomte, C.; Protas, J.; Guilard, R.; Fliniaux, B.; Fournari, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1306. (b) Johnson, J. F.; Scheidt, W. R. *Inorg. Chem.* **1978**, *17*, 1280. (c) Schaverien, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968.

of $[(\mathrm{OEP})\mathrm{Zr}]_2(\mu\text{-OH})_2(\mu\text{-O})$. The Soret band of this compound dissolved in CH_2Cl_2 is hypsochromically shifted to 388 nm compared to the range of values generally found in monomeric porphyrin compounds, in accordance with a dimeric formulation.[10b,31] High resolution EI/MS confirms the parent ion to be the dehydrated species $[(\mathrm{OEP})\mathrm{Zr}]O_2^+$. Treatment of $[(\mathrm{OEP})\mathrm{Zr}]_2(\mu\text{-OH})_2(\mu\text{-O})$ with $SiCl_4$ in refluxing toluene quantitatively produces $(\mathrm{OEP})\mathrm{ZrCl}_2$, thus providing a facile way to recuperate $(\mathrm{OEP})\mathrm{ZrCl}_2$ from hydrolyzed (OEP)Zr derivatives.

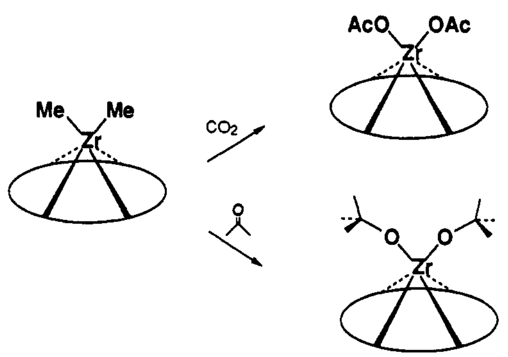
The alkyl compound $(\mathrm{OEP})\mathrm{Zr}(\mathrm{CH_2SiMe_3})_2$ undergoes rapid and clean protonolysis with 2 equiv of *tert*-butanol, acetic acid, or HOTf or a slight excess of HCl to give the corresponding (OEP)Zr dialkoxide, diacetate, ditriflate, or dichloride derivatives, as judged by ^{1}H NMR spectroscopy.

Reactions of (OEP)ZrR$_2$ with Small Molecules. The dialkyl complexes $(\mathrm{OEP})\mathrm{ZrR}_2$ (R = Me, CH_2SiMe_3) react rapidly with CO or *tert*-butyl isocyanide at low temperature; however, only complex mixtures of uncharacterizable products result. In contrast, CO insertions into zirconocene–alkyl[32] and –hydride[2b] bonds are generally quite clean and the resulting η^2-acyl products have been well characterized. In toluene-d_8 at −78 °C, $(\mathrm{OEP})\mathrm{Zr}(\mathrm{CH_2SiMe_3})_2$ reacts instantaneously with ^{13}CO, as judged by the color change from red to orange and the disappearance of signals due to the starting material in the ^{1}H NMR spectrum. These data also indicate reduction of the porphyrin ring symmetry, as judged by the appearance of several new peaks for the inequivalent OEP methyl groups and the meso-hydrogens. The former are shifted upfield, ranging from δ 0.7–1.9 ppm. The most intense peak in the ^{13}C NMR spectrum was observed at δ 87.2 ppm, which is in the range typically encountered for alkoxides. Given the complexity of the reactions described above, it is difficult at present to draw any conclusion as to the constitution of the products or the mechanism(s) involved. Migration of an alkyl or acyl group to the porphyrin ring (which has precedents in late transition metal porphyrin chemistry) is, however, a distinct possibility.[33]

In contrast to the above, reactions of zirconium porphyrin dialkyls with CO_2 and acetone yield clean products that are readily identified. Thus, treatment of (OEP)-ZrMe$_2$ with CO_2 generates the known acetate complex $(\mathrm{OEP})\mathrm{Zr}(\mathrm{OAc})_2$,[10a] whereas reaction with acetone affords the bis(alkoxide) $(\mathrm{OEP})\mathrm{Zr}(\mathrm{O^tBu})_2$, in high yield (Scheme IV).

These reactions proceed rapidly in the dark, and experiments with radical traps such as dihydroanthracene indicate that radicals are not involved. Apart from photochemically induced reactions,[34] CO_2 insertions into metal porphyrin alkyl bonds have, to the best of our knowledge, never been observed. This reactivity should also be compared with the behavior of metallocene derivatives toward these substrates: CO_2 inserts into Zr–C bonds only at high pressure,[35] and insertion of acetone is rare.[36] Floriani and co-workers proposed that insertion of CO_2-like molecules requires prior coordination with concomitant polarization of these substrates.[35] An appealing explanation for the enhanced reactivity of (OEP)Zr vs zirconocene derivatives toward CO_2 and acetone would entail stronger polarization of these unsaturated molecules by the more Lewis acidic (OEP)Zr center.

Scheme IV



Demetalation. Using Buchler's classification system, Zr porphyrins are class II compounds[37] and should not be demetalated by acids such as HCl or acetic acid. Indeed, $(\mathrm{OEP})\mathrm{Zr}(\mathrm{OAc})_2$ is produced in refluxing acetic acid and no trace of the free base porphyrin is generated. In the presence of an excess of KF, however, demetalation of $(\mathrm{OEP})\mathrm{Zr}(\mathrm{OAc})_2$ takes place rapidly and quantitatively (eq 3). This provides a convenient method for regenerating

$$(\mathrm{OEP})\mathrm{ZrR}_2 \xrightarrow[\mathrm{HOAc}]{\mathrm{KF}} \mathrm{H}_2\mathrm{OEP} \qquad (3)$$

$$\mathrm{R} = \mathrm{Cl},\ \text{alkyl, alkoxide, acetate, etc.};\ \mathrm{R}_2 = \mathrm{OEP}$$

the expensive H_2OEP in pure form after Soxhlet extraction with toluene. The facile demetalation under these conditions is no doubt due to the formation of very strong Zr–F bonds.[1]

Summary and Conclusions

Our studies have shown that, in common with the more well-known metallocene moiety Cp_2M, the (OEP)Zr fragment stabilizes a wide variety of ancillary ligands. Results of X-ray studies show that the zirconium is displaced well out of the porphyrin plane with attendant ligands constrained to be cis to each other, therefore highlighting the structural similarities between the early metal porphyrins and metallocenes. Relative to their metallocene analogues, the organometallic porphyrin derivatives are quite reactive toward insertion reactions. At the same time, however, dialkyls with β-hydrogens, such as $(\mathrm{OEP})\mathrm{ZrEt}_2$, appear to be remarkably stable with respect to β-abstraction and other decomposition pathways. As mentioned in our preliminary note, the dialkyl and diaryl porphyrin derivatives are unusual in that they serve as relatively active precatalysts for the hydrogenation of unhindered olefins;

---

[31] Gouterman, M.; Holten, D.; Lieberman, E. L. *Chem. Phys.* **1977**, *25*, 139.

[32] See p 147 in ref 1.

[33] Konishi, K.; Sugino, T.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1991**, *113*, 6487 and references therein.

[34] (a) Cocolios, P.; Guilard, R.; Bayeul, D.; Lecomte, C. *Inorg. Chem.* **1985**, *24*, 2058. (b) Inoue, S.; Takeda, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 984. For the related SO_2 insertions see: (c) Boukhris, A.; Lecomte, C.; Coutsolelos, A.; Guilard, R. *J. Organomet. Chem.* **1986**, *303*, 151. (d) Cocolios, P.; Fournari, P.; Guilard, R.; Lecomte, C.; Protas, J.; Boubel, J. C. *J. Chem. Soc., Dalton Trans.* **1980**, 2081. (e) Guilard, R.; Cocolios, P.; Fournari, P.; Lecomte, C.; Protas, J. *J. Organomet. Chem.* **1979**, *168*, C49.

[35] Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1985**, *24*, 654.

[36] Insertion of CO_2 and acetone into the Zr–C bonds of zirconocene benzyne and related metallacycles is, however, well-known. See ref 3.

[37] Buchler, J. W. In *Porphyrins and Metalloporphyrins*; Smith, K. M.; Ed.; Elsevier: New York, 1975; p 159.

full details will be presented in forthcoming publications. Further work on these interesting compounds is in progress.

Experimental Section

General Considerations. Inert atmosphere glovebox and Schlenk-line techniques were used throughout the preparative procedures.[38] NMR tube experiments were performed either in flame-sealed or Teflon stoppered NMR tubes, unless stated otherwise. Tetrahydrofuran, diethyl ether, hexanes, benzene, pentane, and toluene were all predried over 4-Å molecular sieves and, with the exception of toluene, were all distilled from purple sodium/benzophenone under N_2. Toluene was distilled from sodium under N_2. Dichloromethane and pyridine were predried over 4-Å molecular sieves, degassed by three freeze, pump, and thaw cycles, and distilled from calcium hydride under N_2. Acetone was vacuum transferred from 4-Å molecular sieves and degassed by three freeze, pump, and thaw cycles. All NMR solvents were dried as for their undeuterated counterparts but were purified by vacuum transfer and, additionally, were passed through alumina in the glovebox.

Carbon monoxide, ^{13}CO (96%, ^{13}C), and carbon dioxide (bone dry) were used directly from the cylinder. $ZrCl_4(THT)_2$ and $ZrCl_4(DME)$ were prepared by addition of a stoichiometric amount of the appropriate ligand to $ZrCl_4$ in CH_2Cl_2 followed by precipitation with hexane. COT was vacuum transferred after drying over molecular sieves and degassed by three freeze, pump, and thaw cycles. $Li_2OEP(THF)_4$,[14] $Li_2OEP(DME)_n$,[14] and $LiCH_2SiMe_3$[39] were prepared according to the literature procedure. Li(p-$C_6H_4{}^tBu$) was prepared from the reaction of the aryl chloride with ^nBuLi in hexane.[19] Diethyl ether solutions of Me_2Mg and Et_2Mg were prepared by addition of a stoichiometric amount of dioxane to the commercially available Grignard reagent followed by filtration. All other reagents were obtained from commercial sources and were used as received.

Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected. IR samples, unless stated otherwise, were either prepared as Nujol mulls between CsI or KBr plates or as KBr pellets in an airtight cell. UV/vis spectra were recorded in 0.2-cm quartz cells and are reported in the form λ_{max} in nm (log ϵ). Elemental analyses and mass spectra (EI, 70 eV) were performed within the College of Chemistry, University of California, Berkeley. ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra were recorded at ambient temperatures. Chemical shifts (δ) for ^1H NMR spectra are reported relative to residual protons in the deuterated solvents, for ^{13}C NMR spectra relative to carbons in the deuterated solvent and for ^{19}F NMR spectra relative to trifluoromethylbenzene at δ = 0.0 ppm as external standard. Some of the quaternary carbon signals in the ^{13}C NMR spectra were not observed.

(OEP)ZrCl$_2$·0.5Tol. Method A. DME (225 mL) was added to $Li_2OEP(THF)_2$ (4.51 g, 6.53 mmol) and $ZrCl_4(THT)$ (2.93 g, 9.11 mmol) in a 500-mL round-bottom Schlenk flask fitted with a reflux condenser and argon inlet. After 20 min the reaction mixture was dark bordeaux-red and most of the solid starting materials were dissolved. Soon thereafter a red crystalline solid began to precipitate. The reaction mixture was heated at reflux for 8 h. The mixture was cooled to room temperature, and the volatiles were removed under vacuum. The residue was washed with hexane (5 × 10 mL). Evaporation of the solvent afforded 920 mg (24.4% relative to $Li_2OEP(THF)_2$) of $(OEP)_2Zr$. The dark red, hexane insoluble residue was placed in a Soxhlet thimble and extracted with 100 mL of toluene for 36 h. The filtrate, which already contained some red microcrystalline precipitate, was allowed to slowly cool to room temperature and then to −40 °C. After 24 h, 2.9 g (60%) of purple-red microcrystalline $(OEP)ZrCl_2·0.5Tol$ was obtained after filtration. Mp: 322–324 °C. ^1H NMR ($CDCl_3$): δ 10.61 (s, 4 H, CH), 4.34 (m, 16 H, $C\mathit{H}_2CH_3$), 1.90 (t, 24 H, $CH_2C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$): δ 147.1, 142.8, 102.7, 20.1, 18.2. UV/vis (CH_2Cl_2): 329 (4.26), 400 (5.31), 526 (4.20), 564 (4.50). IR (Nujol): 1626 (w), 1312 (w), 1268 (m), 1214 (w), 1146 (m), 1120 (w), 1055 (s), 1016 (s), 981 (m), 957 (s), 916 (w), 865 (w), 846 (w), 805 (w), 745 (w), 731 (w), 708 (w), 483 (w) cm^{-1}. EI/MS: m/z 694 (M^+, 70%), 657 ($M^+ - 37$, 100%). Anal. Calcd for $C_{39.5}H_{48}Cl_2N_4Zr$: C, 64.03; H, 6.53; N, 7.56. Found: C, 64.38; H, 6.30; N, 7.55.

Method B. CH_2Cl_2 (110 mL) was added to a flask containing $ZrCl_4(DME)$ (1.83 g, 5.65 mmol) and $Li_2OEP(DME)_{2.8}$ (3.82 g, 4.71 mmol). The deep bordeaux-red solution was stirred for 6 h, the solvent was removed in vacuo, and the red solid was washed with DME (60 mL). The remaining solid was dried in vacuo and Soxhlet extracted as above. After 24 h at −40 °C, 2.78 g (80%) of microcrystalline $(OEP)ZrCl_2·0.5Tol$ was obtained after filtration.

(OEP)Zr(OTf)$_2$. Trimethylsilyl triflate (0.14 mL, 0.74 mmol) was added using a syringe to a suspension of $(OEP)ZrCl_2·0.5Tol$ (0.220 g, 0.297 mmol) in toluene (25 mL). The starting material dissolved within 10 min to give a dark red solution. After stirring for 2 h, some precipitate had formed which was redissolved by gently heating the flask. The warm solution was filtered and the supernatant slowly cooled to −40 °C. After 24 h, 0.194 g (71%) of small purple crystals were collected by filtration. Mp: 200 °C dec. ^1H NMR (CD_3CN): δ 10.31 (s, 4 H, CH), 3.90 (m, 16 H, $C\mathit{H}_2CH_3$), 1.80 (t, 24 H, $CH_2C\mathit{H}_3$). ^{13}C NMR (CD_3CN): δ 147.4, 144.7, 113.3, 20.2, 16.6. ^{19}F NMR (CD_3CN): δ 11.79. IR (Nujol): 1330 (2), 1265 (s), 1238 (s), 1215 (s), 1196 (s), 1180 (s), 1145 (m), 1136 (m), 1119 (w), 1056 (m), 1030 (s), 1018 (s), 982 (w), 958 (w), 918 (w), 858 (w), 806 (w), 750 (w), 732 (w), 706 (w), 696 (w), 629 (s), 622 (s) cm^{-1}. EI/MS: m/z 920 (M^+, 100%), 790 ($M^+ - 130$, 35%), 771 ($M^+ - 149$, 10%). Λ_M (MeCN, 1.16 mM): 275 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{44}H_{66}N_4Si_2Zr$: C, 49.50; H, 4.81; N, 6.08. Found: C, 49.50; H, 4.69; N, 5.29.

(OEP)Zr(OAc)$_2$. A solution of $(OEP)ZrCl_2·0.5Tol$ (0.200 g, 0.270 mmol) and NaOAc (0.066 g, 0.810 mmol) in acetic acid (20 mL) was heated at reflux for 12 h. In air, an equal amount of water was added to the hot solution, and the fine red precipitate was washed with five 10-mL portions of water yielding 0.19 g (95%) of product. ^1H NMR ($CDCl_3$): δ 10.50 (s, 4 H, CH), 4.19 (m, 16 H, $C\mathit{H}_2CH_3$), 1.90 (t, 24 H, $CH_2C\mathit{H}_3$), 0.09 (s, 6 H, $O_2CC\mathit{H}_3$). ^{13}C NMR ($CDCl_3$): δ 147.3, 141.5, 101.8, 20.3, 20.0, 18.3. The IR and UV/vis spectral data were identical to literature values.[10a]

(OEP)Zr(OAc)Cl. A suspension of $(OEP)Zr(OAc)_2$ (0.217 g, 0.297 mmol) and Me_3SiCl (82 μL, 0.070 g, 0.643 mmol) in toluene (25 mL) was heated at reflux for 3 h. The solvent was removed under vacuum; the product was extracted with CH_2Cl_2 (10 mL), filtered, and concentrated to 5 mL. Addition of 10 mL of hexane to the warm solution and cooling to −40 °C afforded 0.191 g (91%) of red crystals. Mp: 295 °C dec. ^1H NMR ($CDCl_3$): δ 10.57 (s, 4 H, CH), 4.20 (m, 16 H, $C\mathit{H}_2CH_3$), 1.90 (t, 24 H, $CH_2C\mathit{H}_3$), 0.06 (s, 3 H, $O_2CC\mathit{H}_3$). UV/vis: 332 (4.34), 400 (5.23), 528 (4.29), 564 (4.47). IR (KBr): 2962 (s), 2929 (s), 2871 (s), 1535 (w), 1468 (s), 1454 (m), 1374 (w), 1315 (w), 1260 (m), 1220 (w), 1213 (w), 1146 (m), 1108 (m), 1095 (m), 1055 (m), 1016 (s), 981 (m), 959 (m), 916 (w), 892 (w), 874 (w), 847 (w), 802 (m), 747 (w), 737 (w), 720 (w), 695 (m) cm^{-1}. EI/MS: m/z 716 (M^+, 80%), 681 ($M^+ - 35$, 100%). Anal. Calcd for $C_{38}H_{47}ClN_4O_2Zr$: C, 63.52; H, 6.59; N, 7.80. Found: C, 63.03; H, 6.58; N, 7.58.

(OEP)Zr(OSiMe$_3$)$_2$. Toluene (25 mL) was added to $(OEP)ZrCl_2·0.5Tol$ (0.300 g, 0.405 mmol) and $KOSiMe_3$ (0.104 g, 0.810 mmol). The red solution was stirred for 3.5 h; then the solvent was removed at reduced pressure. The red solid was extracted with hexane (35 mL); the filtrate was concentrated to half its volume and slowly cooled to −40 °C affording 0.210 g (65%) of red crystalline $(OEP)Zr(OSiMe_3)_2$. Mp: 231–231.5 °C. ^1H NMR (C_6D_6): δ 10.50 (s, 4 H, CH), 4.00 (m, 16 H, $C\mathit{H}_2CH_3$), 1.86 (t, 24 H, $CH_2C\mathit{H}_3$), −1.07 (s, 18 H, $SiC\mathit{H}_3$). ^{13}C NMR (C_6D_6): δ 147.5, 142.2, 101.9, 20.2, 18.5, 1.9. UV/vis (hexane): 332 (4.46), 398 (5.35), 530 (4.32), 5.66 (4.62). IR (Nujol): 1317 (w), 1269 (m), 1239 (s), 1217 (w), 1146 (m), 1110 (m), 1057 (m), 1026 (m), 1001

---

[38] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; John Wiley: New York, 1986.

[39] Tessier-Youngs, C.; Beachley, O. T. *Inorg. Synth.* **1986**, *24*, 95.

(s), 958 (s), 929 (s), 850 (m), 835 (s), 802 (w), 747 (m), 732 (w), 720 (w), 696 (m), 679 (w) cm^{-1}. EI/MS: *m/z* 800 (M$^+$, 95%), 785 (M$^+$ − 15, 100%). Anal. Calcd for $C_{42}H_{62}N_4O_2Si_2Zr$: C, 62.87; H, 7.79; N, 6.98. Found: C, 62.91; H, 7.60; N, 7.18.

(OEP)Zr(^{t}Bu)$_2$. A 100-mL round-bottom flask was charged with (OEP)ZrCl$_2$·0.5Tol (0.290 mg, 0.392 mmol) and LiO^{t}Bu (0.068 g, 0.850 mmol) in the glovebox. Toluene (15 mL) was added to the flask via cannula, and the reaction mixture was stirred at room temperature for 16 h. After filtration, the dark red solution was concentrated to 3 mL and hexane (2 mL) was added. Slow cooling of this solution to −40 °C afforded 0.185 g of red microcrystals. Adding 5 mL of hexane to the filtrate and slow cooling gave an additional 0.025 g of microcrystalline product (total yield: 70%). Mp: 208–210 °C. ^{1}H NMR (C_6D_6): δ 10.41 (s, 4 H, CH), 3.98 (m, 16 H, C*H*$_2$CH$_3$), 1.87 (t, 24 H, CH$_2$C*H*$_3$), −0.38 (s, 18 H, OCCH$_3$). ^{13}C NMR (C_6D_6): δ 147.8, 142.1, 101.2, 72.7, 31.0, 20.3, 18.7. UV/vis (CH_2Cl_2): 340 (4.74), 398 (5.83), 530 (4.48), 566 (4.80). IR (Nujol): 1459 (s), 1376 (s), 1351 (m), 1206 (s), 1187 (m), 1055 (m), 991 (s), 955 (m), 844 (m) cm^{-1}. EI/MS: *m/z* 786 (M$^+$, 40%), 695 (M$^+$ − 73, 100%). Anal. Calcd for $C_{44}H_{62}N_4O_2Zr$: C, 68.61; H, 8.11; N, 7.27. Found: C, 68.77; H, 8.15; N, 7.16.

(OEP)Zr(O^{t}Bu)Cl. About 50 mL of CH_2Cl_2 was vacuum transferred onto a mixture of (OEP)ZrCl$_2$·Tol (1.014 g, 1.370 mmol) and LiO^{t}Bu (0.110 g, 1.370 mmol). The reaction mixture was slowly warmed from −35 °C to room temperature over a period of 3 h. The dark purple solution was filtered through a fine porosity frit, and the solvent was evaporated to yield 0.950 g (95%) of pure (OEP)Zr(O^{t}Bu)Cl (as judged by ^{1}H NMR spectroscopy). Analytically pure material was crystallized from toluene at −40 °C. Mp: >300 °C. ^{1}H NMR (CDCl$_3$): δ 10.55 (s, 4 H, CH), 4.20 (m, 16 H, C*H*$_2$CH$_3$), 1.97 (t, 24 H, CH$_2$C*H*$_3$), −0.87 (s, 9 H, OCC*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 147.1, 142.5, 101.6, 28.9, 20.0, 18.4. IR (Nujol): 1354 (s), 1314 (m), 1267 (m), 1229 (w), 1196 (s), 1147 (m), 1110 (w), 1056 (m), 1028 (m), 1014 (s), 977 (m), 955 (s), 913 (w), 873 (w), 850 (m), 804 (w), 785 (w), 722 (m), 701 (w) cm^{-1}. EI/MS: *m/z* 730 (M$^+$, 30%), 695 (M$^+$ − 35, 35%), 657 (M$^+$ − 73, 90%), 534 (M$^+$ − 196, 100%). Anal. Calcd for $C_{40}H_{53}N_4OClZr$: C, 65.58; H, 7.29; N, 7.65. Found: C, 65.55; H, 7.25; N, 7.37.

(OEP)Zr(CH$_2$SiMe$_3$)$_2$. A 100-mL round-bottom Schlenk flask was charged with (OEP)ZrCl$_2$·Tol (0.300 g, 0.405 mmol) and LiCH$_2$Si(CH$_3$)$_3$ (0.076 g, 0.810 mmol). The vessel was wrapped with aluminum foil and degassed, and about 20 mL of benzene was added by vacuum transfer. The reaction mixture was allowed to stir for 4 h at ambient temperature, after which all of the starting material had dissolved to give a deep red solution. The mixture was filtered through a fine porosity frit and the benzene removed under reduced pressure to give pure (OEP)Zr(CH$_2$SiMe$_2$)$_2$ as a dark red powder in quantitative yield. Analytically pure material was obtained by crystallization from hexane at −40 °C. Mp: 190–194 °C. ^{1}H NMR (C_6D_6): δ 10.49 (s, 4 H, CH), 3.94 (m, 16 H, C*H*$_2$CH$_3$), 1.86 (t, 24 H, CH$_2$C*H*$_3$), −1.16 (s, 18 H, SiCH$_3$), −3.82 (s, 4 H, CH$_2$Si). ^{13}C NMR (C_6D_6): δ 148.1, 142.5, 102.4, 55.4, 20.2, 18.5, 2.2. UV/vis (CH_2Cl_2): 333 (4.12), 400 (5.34), 530 (4.06), 568 (4.35). IR (Nujol): 1317 (w), 1269 (m), 1248 (m), 1212 (w), 1146 (m), 1109 (w), 1055 (m), 1016 (s), 978 (w), 955 (s), 912 (m), 891 (m), 852 (s), 816 (m), 748 (m), 716 (m), 698 (m), 675 (w), 597 (w), 501 (w), 450 (w) cm^{-1}. EI/MS: *m/z* 796 (M$^+$, 20%), 709 (M$^+$ − 85, 100%). Anal. Calcd for $C_{44}H_{66}N_4Si_2Zr$: C, 66.19; H, 8.33; N, 7.02. Found: C, 66.55; H, 8.25; N, 7.07.

(OEP)ZrMe$_2$·Tol. CH_2Cl_2 (30 mL) was condensed onto (OEP)ZrCl$_2$·0.5Tol (0.300 g, 0.405 mmol). A solution of Me$_2$Mg in Et$_2$O (1.58 mL of a 0.26 M solution, 0.41 mmol) was slowly added at about −10 °C. Immediately, the starting material dissolved to give a dark red solution; the mixture was warmed to room temperature and stirred for 6 h. The solvent was then evaporated and the product extracted with toluene (40 mL). The filtrate was concentrated to 25 mL, and slow cooling to −40 °C afforded 0.190 mg (63%) of red, crystalline (OEP)ZrMe$_2$·Tol. X-ray quality crystals were obtained by slow cooling of a saturated CH_2Cl_2/hexane (1:1) solution of (OEP)ZrMe$_2$·Tol to −40 °C. Mp: 125 °C dec. ^{1}H NMR (C_6D_6): δ 10.59 (s, 4 H, CH), 3.96 (m, 16 H, C*H*$_2$CH$_3$), 1.80 (t, 24 H, CH$_2$C*H*$_3$), −3.62 (s, 6 H, ZrC*H*$_2$). ^{13}C NMR (C_6D_6): δ 146.8, 142.5, 101.4, 43.9, 20.0, 18.4. UV/vis (CH_2Cl_2): 332 (4.56), 398 (5.37), 532 (4.44), 570 (4.67). IR (Nujol): 1312 (w), 1268 (w), 1212 (w), 1146 (m), 1124 (m), 1108 (m), 1055 (s), 1016 (s), 978 (m), 957 (s), 912 (w), 850 (m), 803 (w), 745 (m), 729 (m), 708 (m), 693 (w) cm^{-1}. Anal. Calcd for $C_{45}H_{58}N_4Zr$: C, 72.43; H, 7.83; N, 7.51. Found: C, 72.34; H, 7.53; N, 8.04.

(OEP)Zr(CH$_2$CH$_3$)$_2$. Toluene (30 mL) was vacuum transferred onto (OEP)ZrCl$_2$·0.5Tol (0.305 g, 0.412 mmol). The solution was warmed to −30 °C, and MgEt$_2$ (1.42 mL of a 0.295 M solution, 0.42 mmol) in Et$_2$O was added via syringe. The reaction mixture was allowed to warm to room temperature and was stirred for 5 h. The solvent was then removed under vacuum and the resulting solid extracted with 15 mL of toluene. Addition of 30 mL of hexane and slow cooling to −40 °C afforded 0.134 g (44%) of purple, crystalline product. Although the compound was always pure, as judged by ^{1}H NMR, the results of several combustion analyses were consistently low in carbon. Mp: 100 °C dec. ^{1}H NMR (C_6D_6): δ 10.59 (s, 4 H, CH), 3.98 (m, 16 H, CC*H*$_2$CH$_3$), 1.81 (t, 24 H, CCH$_2$C*H*$_3$), −2.65 (t, J = 7.6 Hz, 6 H, ZrCH$_2$C*H*$_3$), −3.77 (q, J = 7.6 Hz, 4 H, ZrC*H*$_2$CH$_3$). ^{13}C NMR (C_6D_6): δ 148.6, 142.5, 101.8, 43.5, 20.2, 18.6, 6.1. UV/vis (CH_2Cl_2): 331 (4.48), 400 (5.29), 532 (4.35), 571 (4.59). IR (Nujol): 1308 (s), 1266 (m), 1211 (w), 1170 (w), 1146 (m), 1109 (w), 1057 (m), 1014 (s), 976 (m), 953 (s), 911 (w), 896 (w), 889 (w), 668 (w), 847 (w), 721 (s), 693 (m) cm^{-1}. Anal. Calcd for $C_{40}H_{54}N_4Zr$: C, 70.43; H, 7.98; N, 8.21. Found: C, 68.94; H, 7.26; N, 7.79.

(OEP)Zr(*p*-C$_6$H$_4$^{t}Bu)$_2$. A 100-mL round-bottom Schlenk flask was charged with (OEP)ZrCl$_2$·0.5Tol (0.300 g, 0.405 mmol) and Li(*p*-C$_6$H$_4$^{t}Bu) (0.115 g, 0.820 mmol) in the glovebox. Benzene (30 mL) was added via cannula, the reaction mixture was stirred at room temperature for 1.5 h, and then the solvent was removed under reduced pressure. A ^{1}H NMR spectrum of this crude product showed that it contained approximately 90% (OEP)Zr(*p*-C$_6$H$_4$^{t}Bu)$_2$ along with some starting material and a very small amount of an unidentified side product. All attempts to purify (OEP)Zr(*p*-C$_6$H$_4$^{t}Bu)$_2$ by recrystallization led to decomposition. ^{1}H NMR (CDCl$_3$): δ 10.59 (s, 4 H, CH), 5.83 (d, 4H, C$_6$H$_4$ *m*-H), 3.95 (m, 16 H, C*H*$_2$CH$_3$), 3.44 (d, 4H, C$_6$H$_4$ *o*-H), 1.83 (t, 24 H, CH$_2$C*H*$_3$), 0.61 (s, 18 H, CCH$_3$). IR (KBr): 2962 (s), 2938 (s), 2868 (s), 1634 (s), 1463 (s), 1448 (s), 1374 (m), 1315 (w), 1260 (s), 1214 (w), 1144 (m), 1108 (m), 1093 (m), 1054 (s), 1011 (s), 980 (w), 956 (m), 913 (w), 956 (m), 913 (w), 875 (w), 839 (w), 800 (s) cm^{-1}.

(OEP)Zr(COT). Cyclooctatetraene (0.422 g, 0.405 mmol) was added to a small piece of potassium (0.050 g, 1.279 mmol) in 2 mL of THF. After 24 h the yellow solution of K$_2$COT was filtered onto (OEP)ZrCl$_2$·0.5Tol (0.300 g, 0.405 mmol) in 20 mL of THF. Purple crystals began to precipitate from the stirred solution after 20 min. After 1 h, the mixture was filtered, the crystalline residue was dissolved in CH_2Cl_2 (8 mL), and the resulting solution was filtered and concentrated to 2.5 mL. An equal volume of diethyl ether was added and the solution slowly cooled to −40 °C. After 24 h, 0.056 g (19%) of purple microcrystals were obtained. Mp: 310 °C. ^{1}H NMR (CDCl$_3$): δ 10.39 (s, 4 H, CH), 4.16 (m, 16 H, C*H*$_2$CH$_3$), 2.04 (s, 8 H, C$_8$*H*$_8$), 1.96 (t, 24 H, CH$_2$C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 147.7, 141.5, 100.9, 88.5, 20.0, 18.9. UV/vis (CH_2Cl_2): 400 (5.21), 526 (3.89), 5.64 (4.26). IR (KBr): 2965 (s), 2924 (s), 2864 (m), 1494 (w), 1468 (m), 1452 (m), 1372 (m), 1312 (w), 1261 (m), 1218 (w), 1144 (m), 1110 (m), 1055 (s), 1014 (s), 980 (w), 953 (m), 915 (w), 847 (m), 797 (m), 788 (m), 747 (w), 729 (s), 695 (m), 667 (m) cm^{-1}. EI/MS: *m/z* 726 (M$^+$, 50%), 622 (M$^+$ − 104, 75%). Anal. Calcd for $H_{44}H_{52}N_4Zr$: C, 72.58; H, 7.20; N, 7.69. Found: C, 73.01; H, 7.13; N, 7.42.

[(OEP)Zr]$_2$(μ-OH)$_2$(μ-O). (OEP)Zr(CH$_2$SiMe$_3$)$_2$ (0.100 g, 0.125 mmol) was dissolved in pyridine (20 mL). The flask was opened to air and the solvent allowed slowly to evaporate. After several days 0.071 g (87%) of small crystals that had formed were collected on a frit and washed with hexane. Mp: >300 °C.

Table IV. Summary of Crystallographic Data

	(OEP)ZrCl$_2$·0.5Tol	(OEP)ZrMe$_2$·CH$_2$Cl$_2$	(OEP)Zr(O^{t}Bu)$_2$
formula	$ZrCl_2N_6C_{36}H_{44}(C_7H_8)_{0.5}$	$ZrCl_2N_4C_{39}H_{52}$	$ZrO_2N_4C_{44}H_{62}$
mol wt, amu	741.0	739.0	770.2
cryst size, mm	0.17 × 0.27 × 0.50	0.20 × 0.28 × 0.70	0.25 × 0.25 × 0.55
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	9.870(2)	10.007(3)	12.4441(12)
b, Å	14.143(3)	13.062(4)	13.1594(21)
c, Å	14.498(3)	14.558(3)	13.9541(18)
α, deg	66.257(17)	82.83(2)	89.972(11)
β, deg	88.003(17)	88.24(2)	99.192(9)
γ, deg	79.645(17)	79.98(2)	115.487(11)
vol, Å^3	1820.9(8)	1859.1(12)	2045.7(10)
Z	2	2	2
d_{calcd}, g cm^{-3}	1.35	1.32	1.24
radiation; λ Å	Mo Kα; 0.710 73	Mo Kα; 0.710 73	Mo Kα; 0.710 73
scan mode	θ–2θ	θ–2θ	θ–2θ
2θ range, (deg)	3–45	3–50	3–48
colln range	$+h,\pm k,\pm l$	$+h,\pm k,\pm l$	$+h,\pm k,\pm l$
abs coeff (μ), cm^{-1}	4.8	4.7	3.0
no. of unique reflns	4749	5531	6393
reflns w/	$F^2 > 3\sigma(F^2)$: 4056	$F^2 > 3\sigma(F^2)$: 4697	$F^2 > 2\sigma(F^2)$: 5085
final *R*, R_w	0.0332, 0.074 29	0.0388, 0.0490	0.0354, 0.0421
T, °C	−105	−102	−108

^{1}H NMR (CDCl$_3$): δ 9.61 (s, 4 H, CH), 3.81 (m, 16 H, C*H*$_2$CH$_3$), 1.70 (t, 24 H, CH$_2$C*H*$_3$), −7.56 (s, 2 H, O*H*). UV/vis (CH$_2$Cl$_2$): 389 (5.30), 524 (4.02), 562 (4.39). IR (Nujol): 1266 (m), 1212 (w), 1146 (m), 1109 (w), 1056 (m), 1014 (s), 978 (w), 955 (s), 913 (w), 838 (m), 721 (s), 598 (m) cm^{-1}. EI/MS: *m/z* 1279 (M$^+$, 100%), 695 (M$^+$ − 584, 70%), 680 (M$^+$ − 599, 65%), 639 (M$^+$ − 670, 85%). EI/MS Calcd for $C_{72}H_{88}N_8O_2{}^{90}Zr_2$: 1276.5124. Found: 1276.5130. Calcd for $C_{72}H_{88}N_8O_2{}^{90}Zr^{92}Zr$: 1278.5128. Found: 1278.5146.

Reaction of (OEP)Zr(OAc)$_2$ with SiCl$_4$. (OEP)Zr(OAc)$_2$ (0.200 g, 0.270 mmol) was heated to reflux with SiCl$_4$ (0.100 g, 0.588 mmol) in toluene (15 mL). After 2 h the mixture was cooled to room temperature and the solvent removed under reduced pressure. The solid was extracted with CH$_2$Cl$_2$ (10 mL) and filtered, and the volume was reduced to 3 mL. Addition of 10 mL of hexane afforded 0.175 g (93%) of solvent free (OEP)ZrCl$_2$ (after drying under high vacuum at 80 °C for 6 h).

Reaction of (OEP)Zr(CH$_2$SiMe$_3$)$_2$ with Protic Acids. About 5 mg of (OEP)Zr(CH$_2$SiMe$_3$)$_2$ was dissolved in CDCl$_3$ or benzene-*d*$_6$ and 1 or 1.5 equiv of H$_2$O or 2 equiv of acid (HO^{t}Bu, HOAc, HOTf, HCl) was added by vacuum transfer. In all cases the ^{1}H NMR spectra of the products were identical with authentic samples. ^{1}H NMR data for [(OEP)Zr(μ-O)]$_2$ in (CDCl$_3$): δ 9.40 (s, 4 H, CH), 3.76 (m, 16 H, C*H*$_2$CH$_3$), 1.65 (t, 24 H, CH$_2$C*H*$_3$).

Recuperation of H$_2$OEP. (OEP)Zr(OAc)$_2$ (0.320 g, 0.431 mmol), KF (0.300 g, 5.164 mmol), and NaOAc (0.500 g, 6.095 mmol) were dissolved in acetic acid (5 mL) and heated at reflux for 30 min, resulting in a color change from red to blue. An equal amount of water was added to the hot solution and the mixture allowed to cool to room temperature. The blue powder was filtered, washed several times with water, and air-dried, yielding 0.219 g (95%) of H$_2$OEP. The product is pure by ^{1}H NMR and UV/vis spectroscopy; however, we routinely recrystallized it by Soxhlet extraction with toluene. The procedure is conveniently scaled up to yield up to 15 g of product.

Reaction of (OEP)Zr(CH$_2$SiMe$_3$)$_2$ with CO (^{13}CO). About 5 mg of (OEP)Zr(CH$_2$SiMe$_3$)$_2$ was dissolved in toluene-*d*$_8$ in an NMR tube, the tube was evacuated by three freeze, pump, and thaw cycles, and a slight excess of CO (^{13}CO) was vacuum transferred into the tube at −78 °C. Immediately, the color changed to orange. ^{1}H and ^{13}C NMR spectra were taken at different temperatures, from −78 °C to room temperature.

Reaction of (OEP)ZrMe$_2$ with CO$_2$. About 5 mg of (OEP)ZrMe$_2$ was dissolved in benzene-*d*$_6$ in an NMR tube, and excess CO$_2$ was added via syringe through a serum cap. The ^{1}H and ^{13}C NMR spectra of the product were identical with those of (OEP)Zr(OAc)$_2$. The conversion was greater than 95%. No difference in the reactivity was noticed when the reaction was performed in the presence of 5 equiv of 5,10-dihydroanthracene.

Reaction of (OEP)ZrMe$_2$ with Acetone. To about 5 mg of (OEP)ZrMe$_2$ in benzene-*d*$_6$ in an NMR tube was added 2 equiv of acetone dissolved in benzene-*d*$_6$. The ^{1}H and ^{13}C NMR spectra of the product were identical with those of (OEP)Zr(O^{t}Bu)$_2$. The conversion was greater than 90%.

Structures. Table IV lists a summary of crystallographic data for all three structurally characterized compounds. General operating procedures were as previously described.[40] Crystals were covered with a layer of Paratone-N hydrocarbon oil, removed from the drybox, inspected, and mounted on glass fibers as described by Hope.[41] Structure determinations were carried out by Dr. Hollander, Staff Crystallographer, CHEXRAY, University of California, Berkeley.

(OEP)ZrCl$_2$. Data for (OEP)ZrCl$_2$ were collected at −105 °C. Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry. The 4749 unique raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. A disordered toluene of solvation was discovered and a model included with two full occupancy carbon atoms refined with anisotropic thermal parameters and three half-occupancy carbon atoms included with isotropic thermal parameters. In a difference Fourier map calculated following the refinement of all non-hydrogen atoms, peaks were found corresponding to the positions of most of the hydrogen atoms. Hydrogen atoms were assigned idealized locations and values of B_{iso} 1.2 to 1.3 times the B_{eqv} of the atoms to which they were attached. They were included in structure factor calculations, but not refined. Inspection of the residuals ordered in ranges of (sin θ)/λ, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.57 e/Å^3, and the lowest excursion was −0.11 e/Å^3. There was no indication of secondary extinction in the high-intensity low-angle data.

(OEP)Zr(O^{t}Bu)$_2$. Data for (OEP)Zr(O^{t}Bu)$_2$ were collected at −108 °C. Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry. The 6393 unique raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the

---

(40) Bonasia, P. J.; Arnold, J. *Inorg. Chem.* **1992**, *31*, 2508.

(41) Hope, H. In *Experimental Organometallic Chemistry*; Wayda, A., Darensbourg, M. Y., Eds.; ACS Symposium Series No. 357; American Chemical Society: Washington, DC, p 257.

intensity standards revealed a reduction of 7.3% of the original intensity. The data were corrected for this decay. Due to loss of orientation of the crystal it was not possible to collect azimuthal scan data. An empirical correction based on the differences of F_o and F_c after refinement of all atoms with isotropic thermal parameters was applied to the data ($T_{max} = 1.11$, $T_{min} = 0.86$).[42] The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.2 times the B_{eqv} of the atoms to which they were attached. They were included in structure factor calculations, but not refined. Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.50 e/Å^3, and the lowest excursion was −0.09 e/Å^3. The largest peaks were all located near the Zr atom. There was no indication of secondary extinction in the high-intensity low-angle data.

(OEP)ZrMe$_2$. Data for (OEP)ZrCl$_2$ were collected at −102 °C. Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry. The 5531 unique raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the intensity standards revealed a reduction of 6.7% of the original intensity. The data were collected for this decay. The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. In a difference Fourier map calculated following the refinement of all non-hydrogen atoms, peaks were found corresponding to the positions of most of the hydrogen atoms. Hydrogen atoms were assigned idealized locations and values of B_{iso} 1.2 times the B_{eqv} of the atoms to which they were attached. The methyl hydrogens were located in a difference Fourier map and then adjusted to ideal positions closest to the observed positions. The hydrogens of the dichloromethane were neither observed nor calculated. Hydrogens were included in structure factor calculations, but not refined. Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.67 e/Å^3, and the lowest excursion was −0.08 e/Å^3. There was no indication of secondary extinction in the high-intensity low-angle data.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Exxon Education Foundation for funding.

Supplementary Material Available: Details of the structure determination including tables of temperature factor expressions, positional parameters, intramolecular distances and angles, and least-squares planes (32 pages). Ordering information is given on any current masthead page.

OM930424K

---

(42) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 159.