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Note

High-Vacuum Pyrolysis of Zr(2,3,7,8,12,13,17,18-Octaethylporphyrin)(PhC≡CPh) as a Route to Novel Zr Species: X-ray Structure of a Hetero-Triply Bridged Species, $[(OEP)Zr(\mu\text{-}Cl)]_2(\mu\text{-}O)$

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Introduction

We have had a long-standing interest in synthesis and studies of multiple bonds between transition metals utilizing porphyrins as auxiliary ligands to stabilize M_2^{x+} ($x = 4-6$) cores.[1] While numerous complexes containing multiple bonds between metal atoms of groups 6, 7, and 8 are known in various structural environments, early transition metal (groups 4 and 5) analogues are comparatively rare and are normally restricted to edge- or face-shared bioctahedra or related structural motifs.[2] Recently, successful syntheses of several triply bonded V and Nb dimers of the paddle-wheel geometry have been achieved.[3] In contrast, only singly bonded bridged Zr and Hf dimers are known. The intriguing features of these species include, for example, a possible presence of "super-long" metal−metal bonds (up to 3.6 Å)[4] and the capacity for metal−metal bonding in rather unusual coordination environments, such as peralkylated complexes.[5] Therefore, novel Zr−Zr cores can be expected to provide interesting insights into bonding between early transition metals.

We have had success in the synthesis of novel multiple metal−metal bonds via high-vacuum pyrolysis of suitable metalloporphyrin precursors that contain the metal in the +2 oxidation state. Thermally labile ligands, such as pyridine, alkylphosphines, and diphenylacetylene, can be used to maintain the mononuclearity of the precursors. Recently, the first isolable Zr(II)−porphyrin complex, Zr(OEP)(PhC≡CPh) (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin), was reported.[6] It seemed logical to us to examine the chemistry of this complex under the conditions of high-vacuum solid-state pyrolysis to ascertain its suitability for synthesis of a putative Zr−porphyrin dimer, $Zr_2(OEP)_2$, which might possibly contain a Zr═Zr bond. Herein, we report the results of this study and the solid-state structure of a hydrolysis product, $[Zr(OEP)(\mu\text{-}Cl)]_2(\mu\text{-}O)$. The latter complex contains the novel $[Zr(\mu\text{-}Cl)]_2(\mu\text{-}O)$ core and possesses a number of interesting structural features.

Results and Discussion

Pyrolysis of a highly amorphous solid sample of Zr(OEP)(PhC≡CPh) at 2 μTorr leads to complete loss of the diphenylacetylene within 2 h at 150 °C. The resulting species gives a featureless paramagnetic ^{1}H NMR spectrum, when dissolved in anhydrous C_6D_6 under vacuum. In contrast, under N_2, a single diamagnetic species, **1** (Figure 1), and a paramagnetic background are observed. A dinuclear composition of **1**, Zr(OEP)−X−Zr(OEP), is inferred from the upfield shift of CH_2 and *meso* protons in this complex, relative to those in monomeric Zr(OEP) derivatives, such as $Zr(OEP)Cl_2$ and Zr(OEP)(PhC≡CPh). The nature of the bridging unit is not apparent, although it is tempting to speculate that X may be N_2. Several N_2 complexes of Zr have been prepared by generating a coordinatively unsaturated Zr(II) derivative under an N_2 atmosphere. All complexes have a bridging N_2 unit coordinated either end-on (μ, η^1, η^1)[7] or side-on (μ, η^2, η^2).[8] While **1** shows no absorption in the 2700−1700 cm^{-1} region, the N−N stretch in centrosymmetric Zr(OEP)−X−Zr(OEP) is not expected to be IR active.

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(2) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Calendron Press: Oxford, 1993; pp 593−604. (b) Benard, M.; Rohmer, M. *J. Am. Chem. Soc.* **1992**, *114*, 4785−4790.

(3) (a) Tayebani, M.; Feghali, K.; Gambarotta, S.; Yap, G. P. A.; Thompson, L. K. *Angew. Chem., Int. Ed.* **1999**, *38*, 3659−3661 and references therein. (b) Cotton, F. A.; Matonic, J. H.; Murillo, C. A. *J. Am. Chem. Soc.* **1998**, *120*, 6047−6052. (c) Cotton, F. A.; Timmons, D. J. *Polyhedron* **1998**, *17*, 179−184. (d) Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *Inorg. Chem.* **1993**, *32*, 2881−2885.

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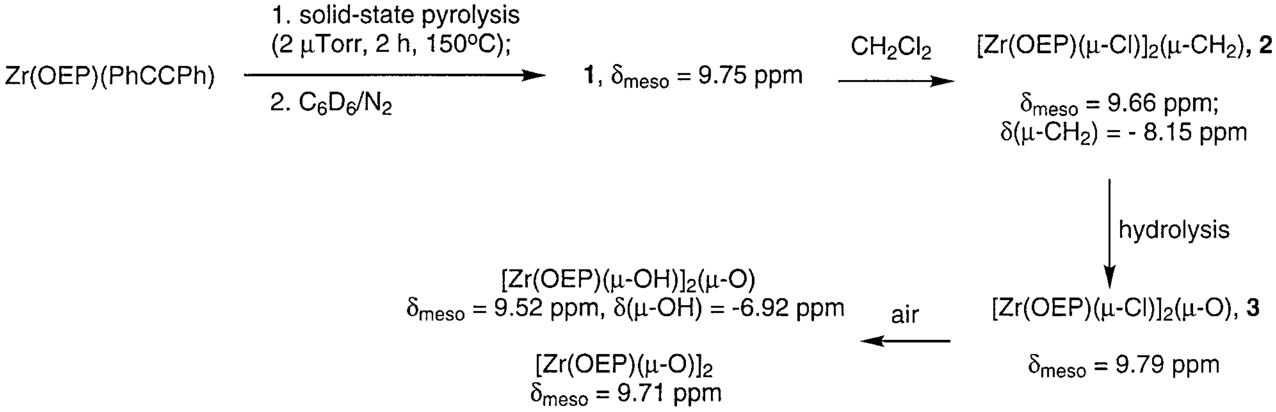

Figure 1. Schematic representation of the transformations observed in the present work; δ_{meso} is the chemical shift of the *meso* protons of the porphyrin ligand. All chemical shifts are given for samples in anhydrous C_6D_6.

Both the original paramagnetic species and diamagnetic complex **1** rapidly decompose at room temperature, yielding several new OEP complexes, even under anaerobic and anhydrous conditions.

A more stable derivative, **2**, is obtained cleanly if the paramagnetic residue after pyrolysis is dissolved in C_6D_6 containing a small amount of CH_2Cl_2 (~0.25% mol, 8 equiv). The ^1H NMR spectrum of product **2** indicates a dinuclear composition (an upfield shift of the resonances of the *meso* protons of the porphyrin core and the CH_2 units of the ethyl substituents) and a bridging unit (or units) containing 2 protons per dinuclear molecule. The latter protons resonate at a significantly higher field (−8.15 ppm in C_6D_6) than do the protons on the bridging hydroxide in $[Zr(OEP)(\mu\text{-}OH)]_2(\mu\text{-}O)$[9] (−6.92 ppm in C_6D_6 and −7.56 ppm in $CDCl_3$),[10,11] indicating that they are bound to an element more electropositive than O, consistent with a methylene bridge. Oxidative addition across a carbon−halogen bond is quite common for Zr(II) derivatives[12] but has also been observed for certain Zr(III)[13] and Zr(IV)−alkyl species.[14] Decomposition of **2**, albeit still rapid, yields a single product **3**, whose composition was unambiguously determined crystallographically as $[Zr(OEP)(\mu\text{-}Cl)]_2(\mu\text{-}O)$. Because the only likely source of Cl atoms in **3** is the preceding reaction with CH_2Cl_2, the composition of **3** supports the assignment of **2** as $[Zr(OEP)(\mu\text{-}Cl)]_2(\mu\text{-}CH_2)$. Apparently, **3** is generated via hydrolysis of the CH_2 unit. Indeed, a number of oxo- or hydroxo-bridged Zr(por) and Hf(por) species have been generated via, usually unintended, hydrolysis of organometallic derivatives.[15] Hydrolysis of methylene and methyl bridging units has been observed for Zr(IV) derivatives in other coordination environments as well.[16] The oxo-bridged dimer **3** is stable in air in the crystalline form, but its solutions undergo a change of color, indicative of further hydrolysis, ultimately yielding a mixture of $[Zr(OEP)(\mu\text{-}OH)]_2(\mu\text{-}O)$ and $[Zr(OEP)(\mu\text{-}O)]_2$ as the major products.

It was reported that the diphenylacetylene ligand in the only known Zr^{II}(por) derivative, $Zr^{II}(OEP)(PhC{\equiv}CPh)$, can be *reversibly* displaced by THF.[6] Likewise, phosphines have been used successfully to stabilize the Cp_2Zr^{II} moiety and related Zr(II) fragments.[17] However, no characterizable species were obtained upon addition of $PhC{\equiv}CPh$ (as a benzene solution) or PEt_3 (neat or as a benzene solution) to the paramagnetic residue obtained in pyrolysis of $Zr(OEP)(PhC{\equiv}CPh)$, suggesting that this novel species may not be a mononuclear Zr(II) derivative. Its paramagnetism indicates a +2 or +3 oxidation state of Zr. In the latter case, Zr(II) present initially has to undergo oxidation during the pyrolysis. Although reaction with $PhC{\equiv}CPh$ is unlikely because sublimation of the intact ligand is observed during pyrolysis (see the Experimental Section), such oxidation could occur

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(7) (a) Manriquez, J. M.; McAlister, D. R.; Rosenberg, E.; Shiller, A. M.; Williamson, K. L.; Chan, S. I.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3078−3083. (b) A much less stable Hf complex is also known: Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97−104.

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(9) Brand, H.; Arnold, J. *Organometallics* **1993**, *12*, 3655−3665.

(10) (a) The only other dinuclear Zr(OEP) derivative reported, $[Zr(OEP)]_2(\mu\text{-}OH)_3(7,8\text{-}C_2B_9H_{12})$, manifests the OH resonance at −7.72 ppm in $CDCl_3$.[10b] Because this complex was not available to us, we were unable to determine the chemical shift of the μ-hydroxo moiety in C_6D_6. However, it probably experiences a downfield shift upon switching to C_6D_6, by analogy with such a shift observed in this work for $[Zr(OEP)(\mu\text{-}OH)]_2(\mu\text{-}O)$. The corresponding resonances in *meso*-substituted analogues occur at slightly lower fields (all in $CDCl_3$): −6.79 ppm in $[(TPP)Zr(\mu\text{-}OH)_2]_2$[11a] and −6.79 ppm in $[Zr(TPP)(\mu\text{-}OH)]_2(\mu\text{-}O)$,[10b] although the latter chemical shift is at variance with that independently reported[11b] (−8.27 ppm) for apparently the same compound. The origin of this discrepancy is not known: in the two independent crystal structure determinations, eclipsed[10b] and partly staggered conformations[11b] were reported; this different solid-state behavior should not be manifested in solution NMR measurements. (b) Kim, H.; Whang, D.; Do, Y.; Kim, K. *Chem. Lett.* **1993**, 807−810.

(11) (a) Huhmann, J. L.; Corey, J. Y.; Rath, N. P.; Campana, C. F. *J. Organomet. Chem.* **1996**, *513*, 17−26. (b) Thorman, J. L.; Guzei, I. A.; Young, V. G.; Woo, L. K. *Inorg. Chem.* **2000**, *39*, 2344−2351.

(12) For a report on a comprehensive study of the reaction of Cp_2Zr^{II}-$(phosphine)_2$ and alkyl halides see: Williams, G. M.; Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 3660−3662.

(13) Cotton, F. A.; Kibala, P. A. *Polyhedron* **1987**, *6*, 645−646.

(14) See for example: Cuenca, T.; Galakhov, M.; Jimenez, G.; Royo, E.; Royo, P.; Bochmann, M. *J. Organomet. Chem.* **1997**, *543*, 209−215.

(15) (a) $[Zr(TPP)(\mu\text{-}OH)]_2(\mu\text{-}O)$: ref in footnote 10. (b) $[Zr(TPP)(\mu\text{-}OH)_2]_2$: ref 11a. (c) $[Hf(TPP)(\mu\text{-}OH)]_2(\mu\text{-}O)$: Ryu, S.; Kim, J.; Yeo, H.; Kim, K. *Inorg. Chim. Acta* **1995**, *228*, 233−236.

(16) See for example: Royo, E.; Galakhov, M.; Royo, P.; Cuenca, T. *Organometallics* **2000**, *19*, 3347−3353.

(17) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687−2695 and references therein.

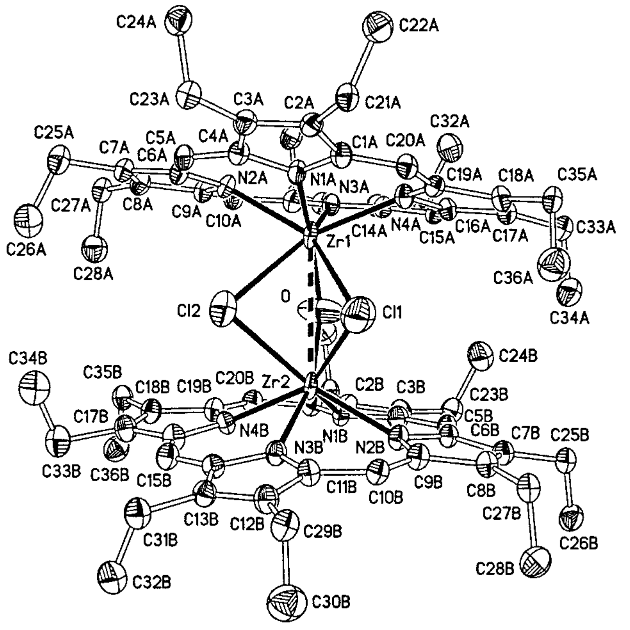

Figure 2. Side-on view of **3**, showing the atom-labeling scheme. The 24-atom porphyrin rings are inclined 18° to each other. The Zr···Zr vector (- ---) lies in the plane of the paper. Anisotropic displacement ellipsoids are drawn at the 40% probability contour level; hydrogen atoms are omitted. Selected interatomic distances (Å) and angles (deg): Zr1−O, 1.900(9); Zr2−O, 1.891(9); Zr1−Cl1, 2.777(4); Zr1−Cl2, 2.694(4); Zr2−Cl1, 2.634(4); Zr2−Cl1, 2.734(4); Zr1−Zr2, 3.317(2); Zr1−O−Zr2, 122.1(5); Zr1−Cl1−Zr2, 75.6(1); Zr1−Cl2−Zr2, 75.3(1); Cl1−Zr1−Cl2, 67.2(1); Cl1−Zr2−Cl2, 68.7(1); O−Zr1−Zr2, 28.9(3); O−Zr2−Zr1, 29.0(3).

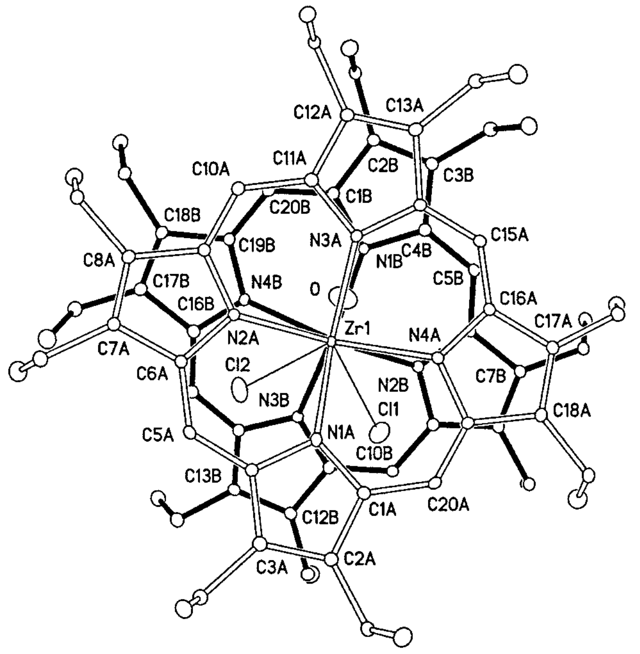

Figure 3. View down the Zr1···Zr2 vector. Molecule B is shown with solid bonds; molecule A (top) is drawn with open bonds. Anisotropic displacement ellipsoids are drawn at the 10% probability level. Relevant parts of the atom-labeling scheme are shown. Hydrogen atoms are omitted.

Table 1. Crystallographic Data for [Zr(OEP)(μ-Cl)]$_2$(μ-O) (**3**)

empirical formula	$C_{72}H_{88}Cl_2N_8OZr_2$
fw	1334.84
lattice params	$a = 18.836(4)$ Å $b = 15.084(4)$ Å $c = 23.170(5)$ Å $\alpha = 90$ ° $\beta = 100.016(5)$ ° $\gamma = 90$ ° $V = 6483(3)$ Å^3
space group	$P2_1/c$ (No. 14)
Z value	4
temp	−94 ± 1 °C
D_{calcd}	1.37 g/cm^3
μ(Mo K$_\alpha$)	4.55 cm^{-1}
radiation	Mo K$_\alpha$ ($\lambda = 0.7069$ Å); graphite monochromated
R1 (wR2)[a]	0.0621 (0.1593)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$.

via reaction with adventitious oxidants in the material of the pyrolytic glassware. Finally, the very high reactivity of this residue is suggestive of a high degree of coordinative unsaturation.[18] Further conclusions regarding its chemical composition or possible structure could not be reached because of its high instability.

Hovewer, **3** was sufficiently stable to allow crystallographic characterization (Figures 2 and 3, Table 1). The two noncoplanar Zr(OEP) moieties are connected by a symmetrical oxygen bridge and two asymmetrically bridging chloride atoms. Whereas several examples of Zr(μ-Cl)$_3$Zr[19] and Zr(μ-O)(μ-Cl)Zr[20] cores are known, the M(μ-Cl)$_2$(μ-O)M unit has so far been observed in only a very few complexes.[21] The latter manifest metric parameters that are comparable to those of the Zr(μ-O)(μ-Cl)$_2$ core (Table 2), although Zr−O bonds in **3** are among the shortest ever observed,[22] indicative of a bond order higher than one, a situation expected for a 14-electron Zr center.

Complex **3** is the first example of a structurally characterized halogen-bridged bismetalloporphyrin derivative[23]and the only Group 4 metalloporphyrin derivative containing bridging atoms other than chalcogens. This results in a number of noteworthy structural differences between **3** and other dinuclear M$_2$(por)$_2$(μ-X) (M = Zr, Hf) species (Table 3). The larger Cl atoms accommodate longer Zr−Cl bonds, which allows for a significantly more open Zr−O−Zr angle,

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(18) Coordinatively saturated Zr(II) complexes, such as Cp*$_2$Zr(phosphine)$_2$, react with chlorohydrocarbons only slowly,[12] as opposed to the rapid formation of **2** in our case.

(19) See for example: (a) [Ph$_4$P][Zr$_2$Cl$_9$]: Chen, L.; Cotton, F. A. *Inorg. Chem.* **1996**, *35*, 7364−7369. (b) (η^6-C$_6$Me$_6$)Zr$_2$Cl$_5$(μ-Cl)$_3$: ref. 31. (c) Zr$_2$(PMe$_3$)$_2$Cl$_5$(μ-Cl)$_3$: Breen, T. L.; Stephan, D. W. *Inorg. Chem.* **1992**, *31*, 4019−4022. (d) Zr$_2$(PPh$_3$)$_2$Cl$_5$(μ-Cl)$_3$: Cotton, F. A.; Kibala, P. A. *Acta Crystallogr.* **1991**, *47*, 270−272. (e) Cp$_2$Zr$_2$Cl$_2$(μ-Cl)$_3^+$: Dias, H. V. R.; Jin, W. *J. Am. Chem. Soc.* **1996**, *118*, 9123; Dias, H. V. R.; Wang, Z. *J. Am. Chem. Soc.* **1997**, *119*, 4650−4655.

(20) Atwood, J. L.; Rogers, R. D.; Bynum, R. V. *Acta Crystallogr.* **1984**, *C40*, 1812−1814.

(21) (a) Friedrich, S.; Gade, L. H.; Li, W.; McPartlin, M. *Chem. Ber.* **1996**, *129*, 1287−1291. (b) Andreu, A. M.; Jalon, F. A.; Otero, A.; Royo, P.; Manotti Lanfredi, A. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans*. **1987**, 953−956. (c) Alcalde, M. I.; Gomez-Sal, P.; Martin, A.; Royo, P. *Organometallics* **1998**, *17*, 1144−1150. (d) Pauls, I.; Weller, F.; Dehnicke, K.; Fenske, D. *Z. Anorg. Allg. Chem.* **1990**, *587*, 61−73. (e) Ta$_2$Cl(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_5$(μ-Cl)$_2$(μ-O) contains a highly unsymmetrical Ta$_2$(μ-Cl)$_2$(μ-O) core: Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *Polyhedron* **1987**, *6*, 1765−1774. (f) Mo$_2$(μ-Cl)$_2$-(μ-O) moiety is present in Cp*$_2$Mo$_2$Cl$_2$(μ-Cl)$_2$(μ-O): Bottomley, F.; Chen, J. *Organometallics* **1992**, *11*, 3404−3411. Metric parameters for this complex are not available because of the poor quality of the crystals. (g) Examples of M$_2$(μ-Cl)$_2$(μ-OX) cores (X = H, alkyl, aryl) are known.

(22) For a compilation of Zr−O and Zr−OX (X = H, alkyl, aryl) bond lengths, see: ref 11b.

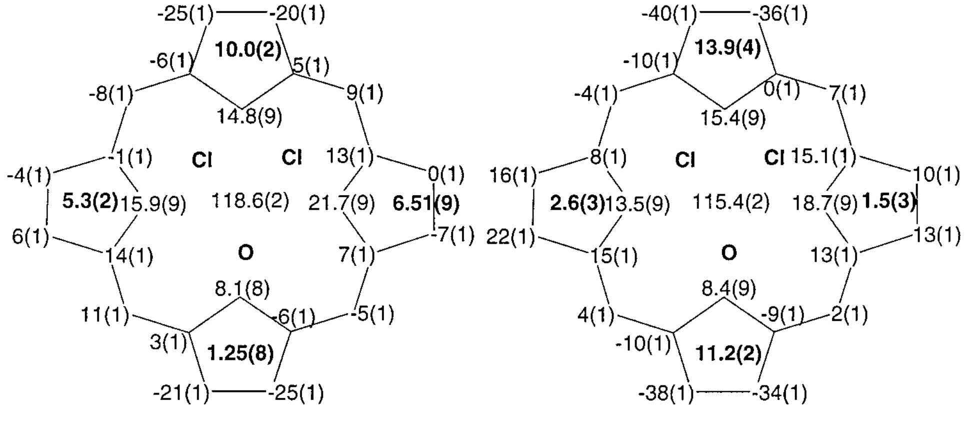
Table 2. Metric Parameters (Å or deg) of the $[Zr(\mu\text{-}Cl)]_2(\mu\text{-}O)$ Unit in **3** and of Related Binuclear Cores

compound	$(M-Cl)_{av}$	$(M-O)_{av}$	$(M-Cl-M)_{av}$	M−O−M	M···M
3	2.710	1.890	75.5	122.1	3.317
$\{[CH_3C(CH_2N(^iPr))_3]Ti\}_2(\mu\text{-}Cl)_2(\mu\text{-}O)$[21a]	2.709	1.841	70.0	115.3	3.110
$[Cl_2(\eta^5\text{-}C_5H_4SiMe_3)Nb]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$[21b]	2.625	1.912	77.4	118.2	3.283
$(NbCl_2)_2[\mu\text{-}(\eta^5\text{-}C_5H_4)_2(Me_2SiOSiMe_2)]\ (\mu\text{-}Cl)_2(\mu\text{-}O)$[21c]	2.647	1.898	77.1	120.9	3.302
$[(PhC{\equiv}CPh)Cl_2W]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$[21d]	2.589	1.898	76.0	114.3	3.188
$[(\eta^1\text{-}NC_4H_4)Cp^*ClZr]_2(\mu\text{-}Cl)(\mu\text{-}O)$[20]	2.665	1.910	82.0	132.5	3.497
$(Cl_3Zr)_2(\mu\text{-}Cl)_3$[19a]	2.574		87.4		3.562
$(\eta^5\text{-}C_6Me_6)Cl_5Zr_2(\mu\text{-}Cl)_3$[31]	2.618		89.3		3.683

Table 3. Metric Parameters (Å or deg) of Select Binuclear Group 4 Metalloporphyrins

compound	$(M-O_{oxo})_{av}$	M−O-M	$(M-N4)_{av}$[a]	M···M	N−M−M−N
3	1.896	122.1	1.084	3.32	8
$[(TTP)Zr(\mu\text{-}O)]_2$[11b]	1.976	101.6	0.97	3.058	22
$[(TPP)Zr(\mu\text{-}OH)]_2(\mu\text{-}O)$[10b]	1.98	101.7	1.06	3.07	8
$[(TPP)Zr(\mu\text{-}OH)]_2(\mu\text{-}O)$[11b]	1.988	100.6	1.04	3.059	22
$[Zr(TPP)(\mu\text{-}OH)_2]_2$ [11a]	2.14[b]	91.4[b]	1.03	3.06	1
$[(TPP)Zr]_2(\mu\text{-}S)_4$[32]			1.044	3.616	0
$[(TPP)Hf(\mu\text{-}OH)]_2(\mu\text{-}O)$[15]	1.98	101.6	1.05	3.06	10

[a] Metal ion displacement from the least-squares plane of the 4 coordinating N atoms. [b] Zr−(μ-OH)−Zr moiety.



Macrocycle A **Macrocycle B**

Figure 4. Relative atom displacements (pm) from the least-squares plane of the 24 atoms of the porphyrin core. Numbers in bold are the angles between the least-squares planes of individual pyrrole rings and the 24-atom plane; numbers in parentheses are esd's.

leading to more effective $\pi_O \rightarrow d_{Zr}$ electronic interaction. As a result of the more open Zr−O−Zr bond angle, and despite the short Zr−O bonds, the Zr···Zr distance is significantly longer than those observed in other oxo-bridged Zr or Hf bismetalloporphyrins. The two porphyrin cores are substantially distorted (Figures 2 and 3), displaying a superposition of three idealized deformations: saddling, ruffling, and doming,[24] each deformation having different contributions for the two macrocycles. The all-positive displacement of N atoms (Figure 4) is indicative of doming, which is a salient feature of porphyrin derivatives of early transition metals, because it leads to an improved overlap between donor orbitals of the pyrrole N atoms and those of the out-of-plane metal ion. Ruffling, which has a proportionally larger contribution in dictating the conformation of macrocycle A, is apparent from alternate displacement of *meso* carbons above and below the 24-atom porphyrin plane. Finally, the saddled deformation manifests itself in alternating displacement of *both* β-carbon atoms of individual pyrrole rings and is particularly pronounced in macrocycle B. The saddled and ruffled deformations are probably necessary to relieve steric interactions between the bridging atoms and the porphyrin cores. Similar forces probably induce the eclipsed conformation of the Zr(OEP) moieties and cause the noncoplanar arrangement of the macrocycles with an unusually large angle between the 24-atom least-squares planes of the porphyrin cores (18°, Figure 2).

In conclusion, high-vacuum pyrolysis of a Zr(II) species, $Zr^{II}(OEP)(PhC{\equiv}CPh)$, leads to the facile loss of the axial ligand and the formation of a highly reactive paramagnetic species. While its properties are not inconsistent with a putative Zr−porphyrin dimer, $Zr_2(OEP)_2$, the very low chemical stability and paramagnetism preclude detailed studies of this species. The studied synthetic route may be

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(23) A crystal structure of a fluoride-bridged *trimer*, (OEP)Ga(μ-F)Ga(OEP)(μ-F)Ga(OEP), was reported (Guilard, R.; Barbe, J.-M.; Richard, P.; Petit, P.; Andre, J. J.; Lecomte, C.; Kadish, K. M. *J. Am. Chem. Soc.* **1989**, *111*, 4684−4687), and a fluoride-bridged ferric heme dimer $((TPP)Fe(\mu\text{-}F)Fe(TPP)BF_4)$ was postulated, but no structural data to support such formulation were given (Cohen, I. A.; Summerville, D. A.; Su, S. R. *J. Am. Chem. Soc.* **1976**, *98*, 5813−5816).

(24) Scheidt, W. R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 3, pp 49−112.

used to generate highly reactive coordinatively unsaturated Zr(por) fragments.

Experimental Section

H_2OEP,[25] $LiN(SiMe_3)_2$, $Li_2(OEP)$,[26] $ZrCl_4(THF)_2$,[27] and Zr(OEP)Cl_2[28] were synthesized as previously described. Attempts to acquire informative MS (+ESI in acetone, acetonitrile, pyridine) were not successful except for $[Zr(OEP)(\mu\text{-}OH)]_2(\mu\text{-}O)$ and $[Zr(OEP)(\mu\text{-}O)]_2$. Synthesis of Zr(OEP)(PhC≡CPh)[6] was modified in the following way: the Mg powder was activated by grinding in a mortar in a drybox; 1.5 equiv were used, and the solids were filtered as soon as the reaction turned green. This method gave higher and more reproducible yields.

1. High-Vacuum Pyrolysis. A pyrolytic glass tube equipped with an O-ring and a valve was flame-dried for at least 5 min under vacuum (~5 mTorr), followed by heating at 200 °C under 5 μTorr for 2 h. The tube was sealed and introduced into a drybox. A sample of Zr(OEP)(PhC≡CPh) (10 mg) was lyophilized by rapid removal of C_6H_6 (5 mL) under vacuum at room temperature, which led to freezing of the solvent. The sublimation of the remaining solid C_6H_6 yielded a highly amorphous brown solid, which was carefully transferred in the pretreated pyrolytic tube. After connecting to a high-vacuum line, the tube was heated for 20 min at 50 °C, after which the temperature was increased to 150 °C and maintained for 2 h. Sublimation of a white solid into the higher parts of the pyrolytic tube was observed during the first 30 min of the reaction. The tube was sealed and introduced into a drybox, and the solids were dissolved in freshly distilled C_6D_6, giving a red solution. UV−vis (toluene, λ_{max}/nm (relative ϵ)): 326 (0.14), 400 (1), 531 (0.09), 566 (0.18). ^1H NMR (C_6D_6): 9.75 (s, 4 H, *meso*), 3.79 (m, 8 H, CH_2), 3.62 (m, 8 H, CH_2), 1.61 (t, 7.5 Hz, 24 H, CH_3) plus paramagnetic background; the latter can be removed by treating the solids with pentane, thereby extracting a purple solid.

2. Analysis of the Product without Exposing to N_2. An NMR tube with a PTFE valve was flame-dried under 5 mTorr for 2 min, followed by heating at 200 °C under 5 μTorr for 1 h and sealing under vacuum. In a drybox, solid Zr(OEP)(PhC≡CPh) (2 mg) was placed in the tube (the sample was not lyophilized, because it was not possible to transfer lyophilized solids into a narrow NMR tube), and the tube was sealed, connected to a high vacuum line, and heated as described above. Upon completion of pyrolysis, the tube was connected to a flask containing a solution of sodium benzophenone ketyl in C_6D_6, and ~400 μL of C_6D_6 was vacuum distilled onto the resulting solid, giving a bluish-purple paramagnetic solution. Diamagnetic OEP-containing species start to appear within 15 min, and complete conversion to a mixture consisting mainly of $[Zr(OEP)(\mu\text{-}O)]_2$ and $[Zr(OEP)(\mu\text{-}OH)_2](\mu\text{-}O)$ with partial precipitation is observed within 1 day in a sealed NMR tube under vacuum.

3. Analysis of the Sublimed Solid. The pyrolysis was conducted for 20 min exactly as described in subsection 1. After the pyrolytic tube was introduced into a drybox, the solid Zr(OEP) residue was dissolved in C_6D_6, and the inside bottom parts of the tube were washed carefully with C_6D_6 without disturbing the white solid sublimate in the upper parts of the pyrolytic tube. The latter was subsequently dissolved in C_6D_6 and gave an ^1H NMR spectrum identical to that of PhC≡CPh. The Zr(OEP)-residue contained unreacted starting material and unidentified species.

4. Reaction with CH_2Cl_2. The solids were generated as described in subsection 1 and dissolved in C_6D_6 containing 0.25% (mol) of CH_2Cl_2. ^1H NMR (C_6D_6): 9.66 (s, 4 H, *meso*), 3.66 (m, 8 H, CH_2), 3.57 (m, 8 H, CH_2), 1.62 (t, 7 Hz, 24 H, CH_3), −8.15 (s, 2 H, μ-CH_2). The complex converts to $[Zr(OEP)(\mu\text{-}Cl)]_2(\mu\text{-}O)$ (**3**) within several hours. UV−vis (toluene, λ_{max}/nm (relative ϵ)): 402(1), 497 (0.03), 531 (0.08), 568 (0.18); the other two dinuclear Zr(OEP) porphyrins,[9] $[Zr(OEP)(\mu\text{-}OH)]_2(\mu\text{-}O)$ and $[Zr(OEP)(\mu\text{-}OH)_2]_2$, show blue-shifted Soret bands, although the analogous TPP complex, $[Zr(TPP)(\mu\text{-}O)]_2$ does not. ^1H NMR (C_6D_6): 9.79 (br s, 4 H, *meso*), 3.83 (m, 8 H, CH_2), 3.67 (m, 8 H, CH_2), 1.65 (t, 7.5 Hz, 24 H, CH_3). IR (KBr): 701 cm^{-1} (Zr−O−Zr). (The stretching bands corresponding to a Zr−O−Zr unit appear at 749−755 cm^{-1} in μ-oxo bridged Cp_2Zr derivatives;[29] such a band appears at 721 cm^{-1} (Nujol) for $[Zr(OEP)(\mu\text{-}OH)]_2(\mu\text{-}O)$.[9]) Crystals suitable for X-ray studies were obtained by layering a toluene solution of **3** with pentane (1:5) at room temperature. To ensure that the species studied crystallographically was representative of the bulk sample, four different batches of crystals were obtained, all showing the same morphology, and three X-ray data sets were collected, all revealing $[Zr(OEP)(\mu\text{-}Cl)]_2(\mu\text{-}O)$. The ^1H NMR spectra of the crystals and the mother liquors indicated the presence of a single species.

5. Other Dimerization Procedures. Some metalloporphyrin dimers can also be obtained via reductive dimerization of the corresponding dichlorides, such as Mo(OEP)Cl_2 and W(OEP)Cl_2, using sodium amalgam, Mg powder, or $Cr^{II}(acac)_2$.[30] The transformation is facile even in toluene, where neither of the reactants is significantly soluble. Because THF, in which reduction of Zr(OEP)Cl_2 with Mg proceeds smoothly, was reckoned to interfere with formation of a Zr−Zr bond, reduction of Zr(OEP)Cl_2 was examined in mesitylene and 2,5-dimethylTHF. The former solvent was chosen on the basis of its reported ability to increase the solubility of polymeric $ZrCl_4$.[31] However, no reaction was observed in mesitylene with either Mg or $Cr^{II}(acac)_2$, probably because of insufficient solubility of Zr(OEP)Cl_2. When the dichloride species was treated with Na/Hg or Mg powder in more polar but noncoordinating 2,5-dimethylTHF, multiple porphyrin derivatives were detected by ^1H NMR in the solution phase, while the solid residue consisted mainly of Zr(OEP)Cl_2. In neither case was a species whose reactivity resembled that of the paramagnetic product obtained via pyrolysis of Zr(OEP)(PhC≡CPh) observed.

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Note Added after ASAP. The version of this paper posted on the Web on December 21, 2001, contained an incorrect formula in the title. The version posted on January 21, 2002, contains the correct formula.

Supporting Information Available: Further experimental details and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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