

Novel low-valent zirconium porphyrin complexes: syntheses, characterization and X-ray crystal structures of (η^5 -cyclopentadienyl)zirconium tetraphenylporphyrin and (η^2 -diphenylacetylene)zirconium octaethylporphyrin

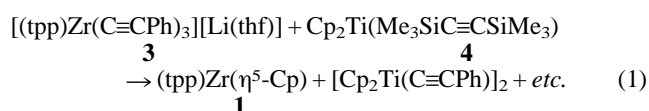
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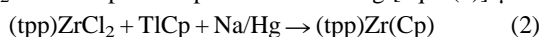
Reactions of (por)ZrCl₂ [por = octaethylporphyrinato (oep) or tetraphenylporphyrinato (tpp) dianion] with TiCp and diphenylacetylene in the presence of Na/Hg or Mg produce novel low-valent zirconium porphyrin complexes (por)Zr(η^5 -Cp) **1** and (por)Zr(η^2 -PhC≡CPh) **2**, respectively; spectroscopic and/or structural data for **1** and **2** are consistent with a formalism in which **1** is a resonance hybrid of a zirconium(III) metal-centered radical and a zirconium(IV) porphyrin radical anion while **2** is a zirconium(II) complex stabilized by a four-electron-donor alkyne ligand.

Low-valent zirconium complexes have led to the development of novel routes to the functionalization of unsaturated organic molecules.¹ For example, zirconium(II) compounds have proved to be effective in converting a variety of enynes and diynes into the corresponding zirconabicycles in zirconocene chemistry.² We and others have been interested in development of zirconium porphyrin chemistry which has been, however, mainly focused on high-valent zirconium(IV) complexes.^{3–5} In fact, there is no well characterized zirconium-(III) or -(II) porphyrin complex except for (oep)ZrCH₂SiMe₃.^{3e} Extremely high sensitivity to air and moisture of such low-valent zirconium porphyrin complexes makes their synthesis and characterization challenging. Here we report the syntheses, characterization and X-ray crystal structures of the novel zirconium-(III) and -(II) porphyrin complexes (tpp)Zr(η^5 -Cp) **1** and (oep)Zr(η^2 -PhC≡CPh) **2**. The former is only the second example of formally zirconium(III) porphyrin complexes and the latter is the first zirconium(II) porphyrin complex.[†]

The cyclopentadienyl complex (tpp)Zr(η^5 -Cp) **1** was first obtained from the reaction of [(tpp)Zr(C≡CPh)₃][Li(thf)] **3**⁶ and Cp₂Ti(Me₃SiC≡CSiMe₃) **4** in toluene [eqn. (1)].⁶



Complex **1** can also be synthesized directly by reacting (tpp)ZrCl₂ with TiCp in the presence of Na/Hg [eqn. (2)].[‡]

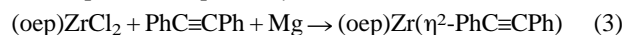


Complex **1** is paramagnetic as indicated by its broad ¹H NMR peaks at δ 22.6, 11.0, 0.6 and -5.0. The mass spectrum of **1** shows a cluster of peaks centered at m/z 767.1 corresponding to the molecular mass of **1**. The structure of **1** was characterized by single crystal X-ray diffraction (Fig. 1).[§] The zirconium ion is coordinated by the four nitrogen atoms of tpp and the η^5 -Cp ligand in a sandwich fashion with the average Zr–N, and Zr–C bond distances being 2.177(10) and 2.49(2) Å, respectively. The four-nitrogen plane and the Cp plane are parallel (dihedral angle, 0.9°). The zirconium atom is 0.773(5) Å displaced out of the four nitrogen plane, and 2.206(6) Å away from the centroid of the Cp ligand. These values are almost the same as those found in (oep)Sc(Cp) (0.80 and 2.196 Å, respectively).⁷

The EPR spectrum of **1** in thf at 77 K is very similar to that of (oep)ZrCH₂SiMe₃.^{3e} It shows a signal typical of a metal-

centered radical, with $g_{\perp} = 2.004$ and $g_{\parallel} = 1.991$ but with no ¹⁴N hyperfine splitting. However, an isotropic signal with $g = 2.001$, typical of an organic radical, is observed at room temperature. The electronic absorption spectrum of **1** recorded at room temperature exhibits a broad band centered at ca. 638 nm which is characteristic for a porphyrin anion radical. The electronic structure of **1** is therefore best described as a resonance hybrid of a zirconium(III) metal-centered radical and a zirconium(IV) porphyrin radical anion, as in the case of (oep)ZrCH₂SiMe₃.^{3e}

The diphenylacetylene complex (oep)Zr(η^2 -PhC≡CPh) **2** was synthesized from the reduction of (oep)ZrCl₂ with equimolar amounts of magnesium in the presence of PhC≡CPh in thf at room temperature [eqn. (3)].[‡]



Product **2** is diamagnetic exhibiting sharp ¹H NMR signals. The ¹H NMR spectrum of **2** is similar to that of the Ti analogue (oep)Ti(η^2 -PhC≡CPh).⁸ The C≡C stretching frequency in **2** observed at 1697 cm⁻¹ is also similar to that of the Ti analogue (1701 cm⁻¹). The η^2 -coordination of the alkyne ligand in **2** has been confirmed by X-ray crystallography (Fig. 2).[§]

The overall appearance of the molecular structure of **2** resembles that of (oep)Ti(η^2 -PhC≡CPh).⁸ A crystallographic two-fold rotation axis passes through the Zr atom and the midpoint of the alkyne C–C bond. The geometry around the Zr atom is square pyramidal, with the four pyrrole nitrogens forming the basal plane and the alkyne triple bond at the apical position. All the metal to ligands distances, Zr–C [2.160(4) Å] and Zr–N [2.203(4), 2.205(4) Å] distances, are longer than the corresponding values for (oep)Ti(η^2 -PhC≡CPh) [Ti–C 2.016(5), 2.015(5) Å; Ti–N 2.083(8)–2.099(7) Å] apparently due to the larger ionic radius of Zr than that of Ti. The metal atom is displaced 0.90 Å out of the mean 24-atom porphyrin plane, which is larger than in the Ti analogue (0.54 Å). The alkyne C–C distance [1.333(8) Å] is comparable to that in the Ti complex [1.30(1) Å]. The bending of the alkyne ligand [C(19)–C(19)–C(20) 133.4(3)°] is more severe than that (143°) in (oep)Ti(η^2 -PhC≡CPh).

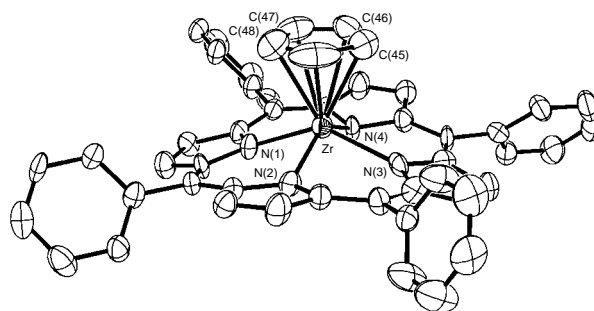


Fig. 1 X-Ray crystal structure of (tpp)Zr(η^5 -Cp) **1**. Selected bond distances (Å): Zr–N(1) 2.183(10), Zr–N(2) 2.190(10), Zr–N(3) 2.169(10), Zr–N(4) 2.166(10), Zr–C(45) 2.47(2), Zr–C(46) 2.51(2), Zr–C(47) 2.50(1), Zr–C(48) 2.47(2), Zr–C(49) 2.50(1).

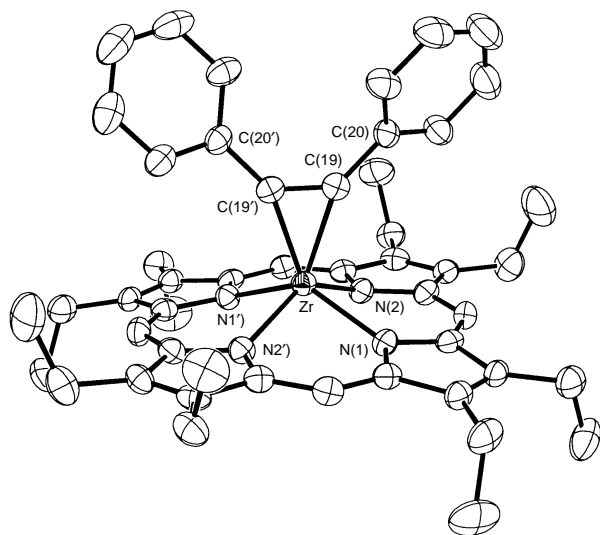


Fig. 2 X-Ray crystal structure of (oep)Zr(η^2 -PhC \equiv CPh) **2**. Selected bond distances (\AA) and angles ($^\circ$) for **2**: Zr–C(19) 2.160(4), Zr–N(1) 2.203(4), Zr–N(2) 2.205(4), C(19)–C(19') 1.333(8), C(19')–C(19)–C(20) 133.4(3), N(1)–Zr–N(1') 138.0(2), N(1)–Zr–N(2), 83.90(14).

Comparison of (oep)Zr(η^2 -PhC \equiv CPh) **2** with Cp₂Zr(η^2 -PhC \equiv CPh)(PMe₃)⁹ supports that the alkyne ligand in **2** behaves as a four-electron donor. According to the 18-electron rule the alkyne ligand is formally a two-electron donor in Cp₂Zr(η^2 -PhC \equiv CPh)(PMe₃). The longer Zr–C distances [2.20(4), 2.25(4) \AA] in Cp₂Zr(η^2 -PhC \equiv CPh)(PMe₃) are in accord with this formalism. The ¹³C chemical shifts for the alkyne carbons in the two complexes are consistent with a two-electron-donor alkyne (δ 141.61, 156.42) in Cp₂Zr(η^2 -PhC \equiv CPh)(PMe₃) and a four-electron-donor alkyne (δ 218.4) in **2**.¹⁰ Taking these into account, the alkyne complex **2** is best described as a zirconium(II) porphyrin complex stabilized by the η^2 four-electron π -donor ligand.

Preliminary reactivity studies of **2** also support the Zr^{II} formalism. Stirring a [²H₈]thf solution of **2** for several hours results in a change to brown. The ¹H NMR spectrum of the resulting solution shows only sharp peaks corresponding to free diphenylacetylene with a broad background. This indicates that the diphenylacetylene ligand is displaced by thf to generate a paramagnetic zirconium porphyrin complex, which has not been fully characterized. When the solvent is removed by evaporation and the residue is taken up in C₆D₆ the original complex **2** is recovered as indicated by ¹H NMR spectroscopy.

In summary, we have synthesized and characterized novel low-valent zirconium porphyrin complexes (tpp)Zr(η^5 -Cp) **1** and (oep)Zr(η^2 -PhC \equiv CPh) **2**. Spectroscopic and/or structural data for **1** and **2** are consistent with a formalism in which **1** is a resonance hybrid of a zirconium(III) metal-centered radical and a zirconium(IV) porphyrin radical anion while **2** is a zirconium(II) complex stabilized by a four-electron-donor alkyne ligand. Further studies on the reactivities of these novel complexes and their utilities in organic and organometallic syntheses are underway.

This work was supported by the Korea Research Foundation (Non Directed Research Fund, 1996) and in part by Center for Biofunctional Molecules.

Footnotes and References

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† Generation of a zirconium(II) porphyrin by photolysis of (tpp)ZrMe₂ has been claimed.^{5b} However, neither its isolation nor characterization was reported to substantiate the claim.

‡ (tpp)Zr(η^5 -Cp) **1**: in a glove box a mixture of (tpp)ZrCl₂ (144 mg, 0.19 mmol), TICp (75 mg, 0.28 mmol) and 6% Na/Hg (150 mg, 0.39 mmol) in thf (ca. 25 ml) was stirred for 1 d at room temp. After the solvent was removed *in vacuo*, the residue was taken up with diethyl ether. Insoluble salts were removed by filtration and the filtrate was concentrated to ca. 5 ml under reduced pressure. The violet crystalline product was filtered and dried *in vacuo* (110 mg, 77%). ¹H NMR (C₆D₆): δ 22.6 (br s, 5 H, Cp), 11.0 (br s, 8 H, H_β), 0.6 (br s, 8 H, Ph), –5.0 (br s, 12 H, Ph). UV–VIS (toluene): λ_{max} (log ϵ) 420 (4.76), 456 (4.10), 544 (3.10), 638 (3.43), 734 (2.91) nm. EPR (thf, 77 K): $g_{\perp} = 2.004$, $g_{\parallel} = 1.991$; (thf, 298 K) $g = 2.001$. FABMS: m/z 767.1 (M⁺). Despite numerous attempts with crystalline products no satisfactory elemental analysis has been obtained owing to extreme air sensitivity of the compound.

(oep)Zr(η^2 -PhC \equiv CPh) **2**. A mixture of (oep)ZrCl₂ (523 mg, 0.75 mmol), Mg powder (50 mesh, 19 mg, 0.78 mmol), and PhC \equiv CPh (135 mg, 0.76 mmol), in thf (ca. 50 ml) was stirred at room temp. in a glove box. The initially purplish red solution turned to dark green within 1 h. After 24 h, the solvent was removed *in vacuo*. The residue was extracted with toluene. The dark red extract solution was filtered and the filtrate was slowly concentrated to ca. 5 ml. Layering pentane (ca. 5 ml) over the solution yielded the microcrystalline product in 2 d, which was filtered, washed with pentane and dried *in vacuo* (329 mg, 54%). ¹H NMR (C₆D₆): δ 10.42 (s, 4 H, *meso*-H), 6.34 (m, 6 H, *m*, *p*-Ph), 4.93 (d, 4H, *o*-Ph), 3.92 (m, 16 H, CH₂CH₃), 1.81 (t, 24 H, CH₂CH₃). ¹³C NMR (C₆D₆): δ 218.4 (C \equiv C), 147.6 (α -pyrrole), 144.2 (β -pyrrole), 132.1 (Ph), 126.9 (Ph), 126.0 (Ph), 125.1 (Ph), 101.5 (*meso*), 20.4 (CH₂), 18.6 (CH₃). IR (KBr): $\nu_{\text{C}\equiv\text{C}}$ 1697 cm⁻¹. UV–VIS (toluene): λ_{max} (log ϵ) 408 (4.70), 458 (2.99), 534 (3.57), 570 (3.76) nm. Anal. Calc. for C₅₀H₅₄N₄Zr: C, 74.85; H, 6.80; N, 6.98. Found: C, 74.83; H, 6.39; N, 6.45%.

‡ *Crystal data*: for **1**: C₄₉H₅₃N₄Zr·C₆H₁₄, $M = 855.19$, triclinic, space group $P1$, $a = 12.647(3)$, $b = 12.821(3)$, $c = 15.499(3)$ \AA , $\alpha = 103.32(3)$, $\beta = 93.65(3)$, $\gamma = 118.97(3)^\circ$, $U = 2093.6(7)$ \AA^3 , $Z = 2$, $\mu(\text{Mo-K}\alpha) = 3.07$ cm⁻¹, $T = 293$ K, Enraf-Nonius CAD4 diffractometer, Mo-K α ($\alpha = 0.71073$ \AA), anisotropic refinement for all non-hydrogen atoms, final cycle of full-matrix least-squares refinement on F^2 with 3896 independent reflections and 493 variables (SHELXL-93), R_1 [$I > 2\sigma(I)$] = 0.0764, wR_2 (all data) = 0.1919, GOF = 1.18. For **2**: C₅₀H₅₄N₄Zr, $M = 802.19$, monoclinic, space group $C2/c$, $a = 15.026(5)$, $b = 19.704(2)$, $c = 15.094(4)$ \AA , $\beta = 106.97(1)^\circ$, $U = 4274(2)$ \AA^3 , $Z = 4$, $\mu(\text{Mo-K}\alpha) = 2.95$ cm⁻¹, $T = 293$ K, anisotropic refinement for all non-hydrogen atoms, final cycle of refinement on F^2 with 2298 independent reflections and 249 variables, R_1 [$I > 2\sigma(I)$] = 0.0462, wR_2 (all data) = 0.0974, GOF = 1.11.

- R. D. Broene and S. L. Buchwald, *Science*, 1993, **261**, 1696; E. Negishi and T. Takahashi, *Acc. Chem. Res.*, 1994, **27**, 124; S. L. Buchwald and R. B. Nielsen, *Chem. Rev.*, 1988, **88**, 1047; P. Binger and S. Podubrin, in *Comprehensive Organometallic Chemistry II*, ed. M. F. Lappert, Elsevier, New York, 1995, vol 4, p. 439.
- E. Negishi, S. J. Holmes, J. M. Tour, J. A. Miller, F. E. Cederbaum, D. R. Swanson and T. Takahashi, *J. Am. Chem. Soc.*, 1989, **111**, 3336; M. Jensen and T. Livinghouse, *J. Am. Chem. Soc.*, 1989, **111**, 4495; W. A. Nugent and D. F. Taber, *J. Am. Chem. Soc.*, 1989, **111**, 6435.
- (a) H. Brand and J. Arnold, *J. Am. Chem. Soc.*, 1992, **114**, 2266; (b) J. Arnold, S. E. Johnson, C. B. Knobler and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1992, **114**, 3996; (c) H. Brand and J. Arnold, *Organometallics*, 1993, **12**, 3655; (d) H. Brand, J. A. Capriotti and J. Arnold, *Organometallics*, 1994, **13**, 4469; (e) H. Brand and J. Arnold, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 95.
- H.-J. Kim, D. Whang, K. Kim and Y. Do, *Inorg. Chem.*, 1993, **32**, 360; H.-J. Kim, D. Whang, Y. Do and K. Kim, *Chem. Lett.*, 1993, 807; S. Ryu, D. Whang, H.-J. Kim, K. Kim, M. Yoshida, K. Hashimoto and K. Tatsumi, *Inorg. Chem.*, in press.
- (a) K. Shibata, T. Aida and S. Inoue, *Tetrahedron Lett.*, 1992, **33**, 1077; (b) K. Shibata, T. Aida and S. Inoue, *Chem. Lett.*, 1992, 1173.
- H.-J. Kim, S. Jung, D. Whang, Y.-M. Jeon and K. Kim, manuscript in preparation.
- J. Arnold and C. G. Hoffman, *J. Am. Chem. Soc.*, 1990, **112**, 8620.
- L. K. Woo, J. A. Hays, R. A. Jacobson and C. L. Day, *Organometallics*, 1991, **10**, 2102; L. K. Woo, J. A. Hays, V. G. Young, C. L. Day, C. Caron, F. D'Souza and K. M. Kadish, *Inorg. Chem.*, 1993, **32**, 4186.
- T. Takahashi, D. R. Swanson and E. Negishi, *Chem. Lett.*, 1987, 623.
- J. L. Templeton, *Adv. Organomet. Chem.*, 1989, **29**, 1.

Received in Cambridge, UK, 21st July 1997; 7/05181F