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**A Metalloporphyrin-Carborane Sandwich Compound: Synthesis and X-ray Crystal Structure of (OEP)Zr( $\eta^5$ -1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)**

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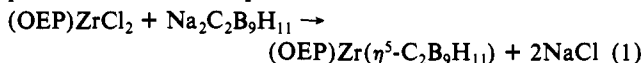
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Metalloporphyrins containing a wide variety of metal centers, cluster geometries, and coligands have been studied in recent years.<sup>1-10</sup> The recent synthesis of metalloporphyrin- $\eta^5$ -cyclopentadienyl compounds of scandium<sup>11</sup> suggested to us that  $\eta^5$ -7,8-dicarbolide-containing species related to these compounds should be at least as stable. Compounds containing both a porphyrin and a carborane have been studied previously,<sup>12</sup> in particular for their potential use in biochemical applications such as boron neutron capture therapy.<sup>13</sup> We sought to extend this chemistry to what we believed would be a synthetically much simpler and more versatile approach, wherein the carborane and porphyrin ligands were bound to the same metal in a novel sandwich structure. We now describe the first example of a such a compound, the  $\pi$ -sandwich species (OEP)Zr( $\eta^5$ -7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>) (OEP = dianion of octaethylporphyrin). It is interesting to note that bis-porphyrin sandwiches Zr(por)<sub>2</sub><sup>14,15</sup> and the zirconacarborane [Zr(1,6-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>)<sub>2</sub>]<sup>2-</sup><sup>16</sup> have been reported previously.

The simple metathesis reaction between (OEP)ZrCl<sub>2</sub><sup>17</sup> and the 7,8-dicarbolide anion<sup>18</sup> [*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>2-</sup> in refluxing THF proceeds as shown in eq 1.



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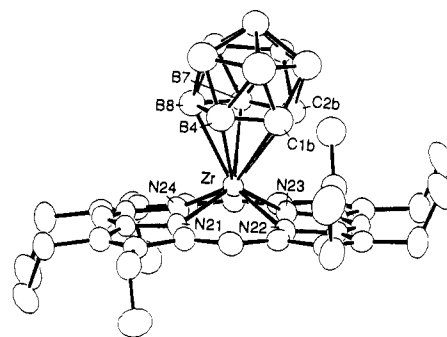
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**Figure 1.** ORTEP view of the molecular structure of (OEP)Zr( $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>). Selected distances (Å) and angles (deg): Zr-N(av), 2.214 (4); Zr-C1B, 2.586 (9); Zr-C2B, 2.549 (7); Zr-B4, 2.539 (10); Zr-B7, 2.482 (8); Zr-B8, 2.488 (9); N21-Zr-N23, 132.1 (2); N22-Zr-N24, 131.5 (2); N22-Zr-C1B, 75.5 (2); N24-Zr-C1B, 153.0 (2).

The product precipitated from the reaction solution over the course of several hours; recrystallization from dichloromethane/diethyl ether afforded the material as an analytically pure dichloromethane solvate in 74% yield. It is insoluble in hydrocarbons, but crystallizes as large dark red needles from a variety of polar solvents such as dichloromethane, acetonitrile, and pyridine. The complex is air-stable as a solid or in solution and may be heated to over 480 °C without melting or noticeable decomposition. It has been fully characterized by MS, NMR spectroscopy, and X-ray crystallography.<sup>19</sup>

In the EI MS, the highest mass peak corresponds to the parent ion at *m/e* 755 followed by loss of the carborane fragment to give the base peak at *m/e* 622 [(OEP)Zr<sup>+</sup>]. A very strong B-H stretch at 2514 cm<sup>-1</sup> in the infrared spectrum is in the usual range for typical carborane complexes containing the ( $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>) ligand.<sup>1</sup> Multinuclear NMR spectroscopy provided valuable evidence for the solution structure of the compound. As expected, the methylene protons of the OEP ligand are diastereotopic and give rise to two complex multiplets centered at  $\delta$  4.1 ppm in the <sup>1</sup>H NMR spectrum. For the carborane ligand, the two CH groups appear as a singlet at -2.84 ppm. This is an unusually high-field resonance for this signal, which is typically found around 2-4 ppm. However, we note that upfield shifts of a similar magnitude are found for the  $\eta^5$ -cyclopentadienyl ligands in the related (OEP)Sc( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>) derivatives<sup>11</sup> and are attributable to shielding by the aromatic OEP ligand. A broad upfield signal centered at -3.4 ppm is assigned to the three BH protons of the C<sub>2</sub>B<sub>9</sub>H<sub>5</sub> ring, whereas the remaining BH signals appear as a very broad resonance at  $\delta$  0.5 ppm. There are no extraordinary shifts in either the <sup>13</sup>C or <sup>11</sup>B NMR spectra. Thus, the <sup>13</sup>C{<sup>1</sup>H} spectrum of the sandwich complex shows a broad, weak singlet at  $\delta$  49.0 ppm due to the carborane carbons along with the usual OEP signals. The usual five-peak pattern commonly observed for  $\eta^5$ -7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> derivatives was seen in the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum.<sup>7</sup> Conclusive evidence for the pentahapto sandwich structure was obtained by X-ray crystallography (Figure 1).<sup>20</sup>

Crystals suitable for X-ray diffraction were grown from dichloromethane/pyridine. The zirconium occupies the 12th vertex

(19) Selected characterization data for (OEP)Zr( $\eta^5$ -C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>): UV/vis  $\lambda$  (log  $\epsilon$ ) (10<sup>-5</sup> M, CH<sub>2</sub>Cl<sub>2</sub>) 400 (4.4), 526 (3.2), 564 (3.6); mp >480 °C; IR (Nujol mull) 2514 vs ( $\nu_{B-H}$ ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 10.65 (s, 4 H), 4.29 (m, 8 H), 4.15 (m, 8 H), 1.89 (t, 24 H), 0.4 (v br), -2.84 (s, 2 H), -3.4 (v br); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 147.8, 144.3, 102.6, 49.0, 20.2, 18.3; <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>, referenced to external BF<sub>3</sub>·Et<sub>2</sub>O at 0 ppm) -0.276, -5.475, -11.61, -14.36, -22.99. Anal. Calcd for C<sub>38</sub>H<sub>25</sub>B<sub>9</sub>Cl<sub>0.5</sub>N<sub>4</sub>Zr: C, 59.1; H, 7.19; N, 7.20. Found: C, 58.8; H, 7.52; N, 7.63.

(20) Crystal data for ZrB<sub>9</sub>N<sub>4</sub>C<sub>38</sub>H<sub>25</sub>: space group  $P\bar{1}$  with *a* = 10.966 (2), *b* = 12.707 (2), *c* = 14.832 (2) Å;  $\alpha$  = 83.501 (4),  $\beta$  = 85.314 (5),  $\gamma$  = 78.316 (4)°; *V* = 2007 Å<sup>3</sup>, *d*<sub>calcd</sub> = 1.26 g cm<sup>-3</sup>, and *Z* = 2. Data were collected at 25 °C with Mo K $\alpha$  ( $\lambda$  = 0.7107 Å) and  $2\theta$  = 45°. A total of 5784 unique data were collected. The structure was solved by Patterson methods and refined by least-squares and Fourier techniques using 438 variables against 3915 data, for which *F*<sup>2</sup> > 3 $\sigma$ (*F*<sup>2</sup>), to give *R* = 5.2%, *R*<sub>w</sub> = 6.2%, and GOF = 1.67. The crystal structure was determined at UCLA.

of the carborane icosahedron and is bonded to two carbon and three boron atoms at distances of 2.586 (9), 2.549 (7), 2.539 (10), 2.482 (8), and 2.488 (9) Å, respectively. The bonding face of the 7,8-dicarbonyl ligand is planar to within 0.012 (9) Å, and the four-nitrogen plane of the OEP ligand is exact within experimental error (0.005 (4) Å). The latter completes the coordination about Zr at distances ranging from 2.209 (4) to 2.217 (4) Å. The zirconium lies 0.904 Å from the nitrogen plane and 2.096 Å from the C<sub>2</sub>B<sub>9</sub> ligand face. The carborane ligand is tilted with respect to the porphyrin ring such that the normals to the two bonding faces form an angle of 4.9°. In the absence of any compelling electronic arguments, we ascribe this distortion to crystal packing effects.

We are currently studying the reactivity of this compound and are looking to extend this synthetic strategy to a variety of related porphyrin and carborane systems.

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**Supplementary Material Available:** Listings of details of the structure determination, including tables of crystal and data collection parameters, temperature factor expressions, positional parameters, intramolecular distances and angles, and least-squares planes (15 pages); listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

## Second-Harmonic Generation from Hyperpolarizable Amphiphiles at Polymer–Polymer Interfaces

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To exhibit second-harmonic generation (SHG; frequency-doubling of light), and other useful second-order nonlinear optical (NLO) properties, a material must contain hyperpolarizable moieties that are arranged in noncentrosymmetric (i.e., oriented) fashion. Such an arrangement can occur in bulk samples that spontaneously form noncentrosymmetric crystals or liquid crystals or that have been "poled" in strong electric fields, or in oriented thin films, whether self-assembled or deposited from an aqueous/air interface.<sup>1,2</sup> Some problems observed with these current techniques include, in the preparation, use of expensive chemicals or apparatus (e.g., Langmuir–Blodgett trough); in the final material, physical delicateness, instability of molecular orientation over time, and intractability toward forming into a waveguide or other thin-film device. We report here the preparation, by a relatively inexpensive and simple spin-coating technique, of physically robust SHG-active samples in which amphiphilic hyperpolarizable molecules are permanently oriented and protected at the interface between solid layers of hydrophobic and hydrophilic polymers.

Hyperpolarizable dyes 1–3 were synthesized and characterized according to the literature.<sup>3</sup> Poly(ethylene-co-maleic acid)

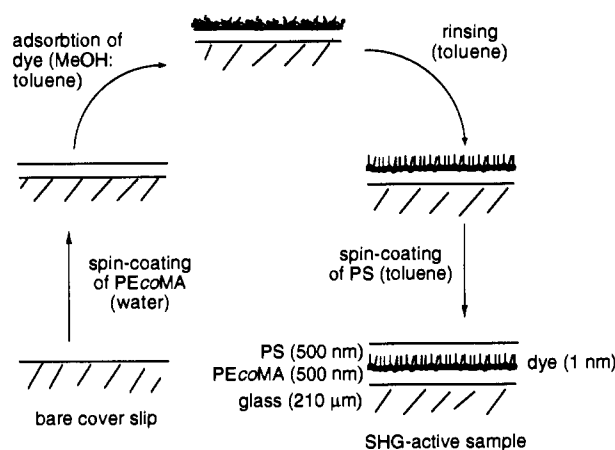
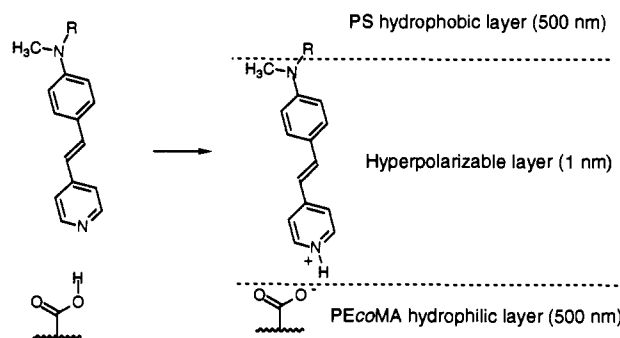


Figure 1. Preparation of samples for SHG testing.

### Scheme I



- 1, R = CH<sub>3</sub>
- 2, R = (CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>
- 3, R = (CH<sub>2</sub>)<sub>17</sub>CH<sub>3</sub>

(PEcoMA) solution was prepared by dissolving 10% w/w of commercial 1:1 ethylene/maleic anhydride copolymer (Aldrich Inc. "Tm 235°") in distilled water and filtering through a 0.45-μm membrane. Samples for SHG measurements were prepared thus (Figure 1): a few drops of PEcoMA solution were placed on a circular glass cover slip (Fisher, 18 mm × 0.21 mm), which was then spun at 3000 rpm for 1 min and then dried in vacuo, to give a smooth and uniform clear coating typically 0.5 μm thick (Dektak profilometer). The film was then wetted with 5–10 drops of dye solution (0.3–0.9% w/w in 1:9 MeOH/toluene), spun dry, rinsed with toluene, and then dried by spinning and in vacuo. A clear 1/2-μm layer of polystyrene ("PS"; Sp<sup>2</sup> Inc. "45,000 g/mol") was then applied in similar fashion from a filtered 10% w/w toluene solution.

Scanning electron micrographs (75000×, Au + Pd coating), from above and in cross section, show the surface of PEcoMA films to be very flat and smooth both before and after application of dye. The change in color from yellow to red-orange confirms protonation of the basic dye as it bonds (ionically) to the acidic hydrophilic polymer; this "chemisorbed" species tenaciously remains while excess free dye easily washes away with toluene. The absorbance of the final colored film at λ<sub>max</sub> (470 nm) can be adjusted from 0.03 to 0.4 with increasing content of dye and/or methanol in the coloring solution. Contact angles θ of treated PEcoMA films, measured on 1-μL sessile drops of distilled water using a home-made video apparatus within 4 s of application (PEcoMA alone, 35–40°; 1 on PEcoMA, 50–55°; 2 on PEcoMA, 75–80°; 3 on PEcoMA, 85–90°), indicate a "tails up" orientation of 2 and 3 even without overlaying polystyrene.

SHG measurements were made using s or p linear polarized light from a Q-switched Nd:YAG laser (1064 nm, 10-ns pulse

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