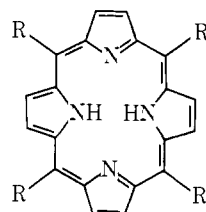


### meso-Tetracarboranylporphyrins

Sir:

There is currently interest in the development of porphyrin based catalysts for the reversible multielectron reduction of small molecules such as  $O_2$  and  $N_2$ . One approach focuses on "face-to-face"<sup>1</sup> or "cofacial"<sup>2</sup> diporphyrins where it is suggested that two metal atoms might act in concert to bind and reduce  $O_2$  or  $N_2$  in the gap between the porphyrin rings.<sup>1</sup> In an alternative approach, we speculate that certain metal complexes attached to a metalloporphyrin can transmit reducing equivalents through the ligand superstructure or by proximity to a molecule bound at the metalloporphyrin center. Peripheral electron-transfer processes previously have been implicated in hemoprotein redox reactions.<sup>3,4</sup> We report here the preparation and characterization of some carboranylporphyrins which represent a first step toward metal-complex-substituted metalloporphyrins which retain a pocket capable of binding small molecules. In principle, certain of these new carbonanylporphyrins are also capable of placing 1-4 metal centers within close proximity of each other and/or the binding pocket.

The meso-tetracarboranylporphyrins **1b-f** have been prepared and characterized, but the synthesis of **1a**,  $H_2T(o-Cb)P$ ,<sup>5</sup> was not successful in our hands.



- 1a**, R = 1,2- $C_2B_{10}H_{11}$   
**b**, R = 1- $CH_2$ -1,2- $C_2B_{10}H_{11}$   
**c**, R = 1- $CH_2$ -2- $CH_3$ -1,2- $C_2B_{10}H_{10}$   
**d**, R = (7- $CH_2$ -8- $CH_3C_2B_9H_{10}$ )<sup>-</sup> $C_5H_9NH_2^+$   
**e**, R = (7- $CH_2$ -8- $CH_3C_2B_9H_{10}$ )<sup>-</sup> $NMe_3^+$   
**f**, R = 1-[*o*- $C_6H_4NHC(O)CH_2$ ]-1,2- $C_2B_{10}H_{11}$

A Rothmund condensation reaction<sup>6</sup> was used in all cases except **1f**. In the case of our attempt at  $H_2T(o-Cb)P$  the aldehyde (1-CHO-1,2- $C_2B_{10}H_{11}$  (**2**)) was prepared by the ozonolysis<sup>7</sup> of 1- $CH_2=CH$ -1,2- $C_2B_{10}H_{11}$ .<sup>8</sup> Treatment of **2** with pyrrole in refluxing  $EtCO_2H$ <sup>6</sup> gave no porphyrinic products detectable by visible spectroscopy, fluorescence, or TLC. Mass spectroscopy suggested partial condensation but no cyclization (maximum observed *m/e* 732, probably  $H[(C_4H_3N)-C(C_2B_{10}H_{11})]_3(C_4H_3N)$ ). Space-filling models<sup>9</sup> indicate that the steric bulk of an icosahedral carboranyl group directly attached to the meso position of the porphyrin could make cyclization difficult.

To investigate the possibility of relieving the steric strain of  $H_2T(o-Cb)P$ , 1- $CH_2CH(O)$ -1,2- $C_2B_{10}H_{11}$  (**3**) was prepared.

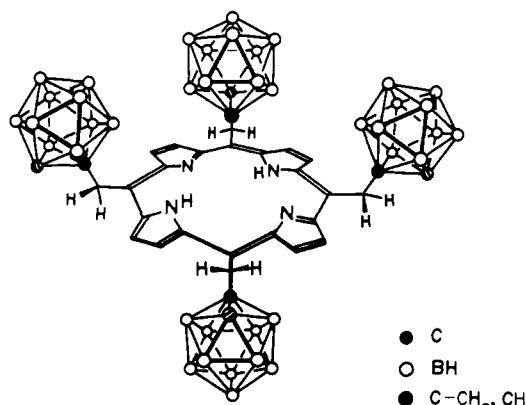
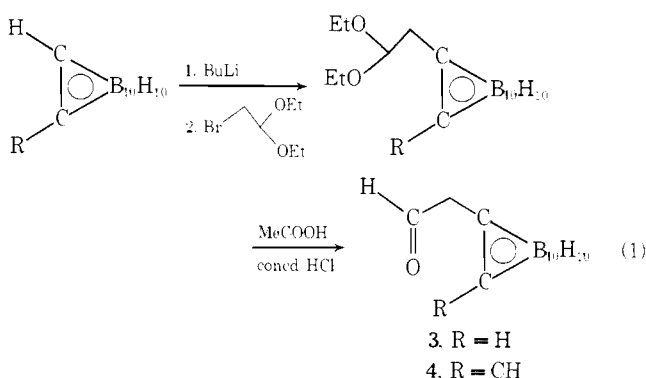


Figure 1. The proposed  $\alpha,\alpha,\alpha,\beta$  atropisomer of  $H_2T(o-CbMe)P$  and  $H_2T(o-MCbMe)P$ . **1b** and **1c**, respectively.

**3** was obtained in 85% overall yield from 1,2- $C_2B_{10}H_{12}$  as shown in eq 1.<sup>10</sup>

The reaction of **3** with pyrrole in  $EtCO_2H$  gave a dark mixture from which  $H_2T(o-CbMe)P$  (**1b**) failed to crystallize. However, **1b** was isolated in 1% yield after column chromatography (silica gel,  $CHCl_3$ ) and recrystallization from acetone- $CHCl_3$ .

The formulation **1b** is based on elemental analysis,<sup>11</sup> visible spectroscopy (665, 595, 550, 518, 420 (Soret) nm), infrared (KBr)  $\nu_{BH}$  2560,  $\nu_{CH}$  (carborane) 3065, and  $\nu_{NH}$  3320  $cm^{-1}$ . The  $^1H$  NMR spectrum of **1b** gave the anticipated signals (in acetone- $d_6$ ,  $\delta$  (intensity), assignment 9.85 (4,  $\beta$ -pyrrole), 6.36 (4, meso- $CH_2$ ), 4.8 (1, carborane CH), -2.7, -2.9 (1, NH)). Included in the relative intensity data are smaller peaks ranging  $\delta \sim 0.6$  upfield from both the  $\beta$ -pyrrole and meso- $CH_2$  peaks. The multiple peaks are probably due to atropisomers.<sup>12</sup> However, we have not yet been able to separate any pure atropisomers of **1b** by column or thin layer chromatography on alumina or silica gel. The proposed structure of one atropisomer of  $H_2T(o-CbMe)P$  is shown in Figure 1.

$H_2T(o-MCbMe)P$  (**1c**) was obtained in the same manner as  $H_2T(o-CbMe)P$  by using the aldehyde 1- $CH_3$ -2- $CH_2CH(O)$ -1,2- $C_2B_{10}H_{10}$  (**4**); **4** was prepared from 1- $CH_3$ -1,2- $C_2B_{10}H_{11}$  using the scheme shown in eq 1. The Rothmund condensation of **4** gives a dark purple product which precipitates from the reaction mixture in pure form in 11% yield. Both **1b** and **1c** failed to give a mass spectrum by conventional electron-impact techniques. However, the molecular weight of **1c** was established by electron impact-desorption<sup>13</sup> at 450  $^\circ C$ . Calcd for  $^{12}C_{36}^{14}H_{70}^{10}B_7^{11}B_{33}^{14}N_4$ : 991.9576. Found: 991.9599. Calcd for  $^{12}C_{36}^{14}H_{70}^{10}B_{10}^{11}B_{30}^{14}N_4$ : 988.9685. Found: 988.9606. The parent envelope centered at *m/e* 991 was the base peak in the spectrum and cutoff at 998 ( $^{12}C_{36}^{14}H_{70}^{11}B_{40}^{14}N_4$ ). The major fragmentation corresponded to loss of the meso substituent.  $H_2T(o-MCbMe)P$  gave a visible spectrum (in acetone, 664, 592, 545, 516, 417 (Soret) nm), infrared ( $\nu_{BH}$  2555,  $\nu_{NH}$  3317), and  $^1H$  NMR consistent with the porphyrin formulation (in  $Me_2SO-d_6$ ,  $\delta$  (intensity), assignment 10.0 (4,  $\beta$ -pyrrole), 6.3 (4, meso- $CH_2$ ), 2.9 (6, carborane  $CH_3$ ), -3.0, -3.1 (1, NH); in pyridine- $d_5$  the spectrum was qualitatively the same but most resonances were multiple, probably owing to atropisomers as explained for **1b**).

Although pure atropisomers of **1b** and **1c** haven't been obtained, preliminary metalation experiments were performed on mixtures.  $H_2T(o-CbMe)P$  was easily metalated with  $ZnCl_2$  or  $Cu(OAc)_2$  in hot DMF as evidenced by visible spectroscopy (in acetone for Zn, 635, 563, 426; for Cu, 636, 550, 420 nm).  $H_2T(o-MCbMe)P$  is readily metalated with  $FeCl_2$  in hot DMF and gives the ferric porphyrin  $ClFe[T(o-MCbMe)P]$  (**5**), upon precipitation from DMF with dilute HCl in air

(visible spectrum of **5**, 677, 644, 575, 508, 417 nm; that for ClFe(TPP),<sup>14</sup> 687, 660, 573, 506, 412 nm). However, it appears that the  $\mu$ -oxo-bridged dimer [T(*o*-MCbMe)P]-Fe<sup>III</sup>OFe<sup>III</sup>[T(*o*-MCbMe)P] (**6**) is formed quantitatively by chromatography of **5** on alumina in CHCl<sub>3</sub> in air (compare visible spectrum of **6** (CHCl<sub>3</sub>), 650, 565, 420, with that of (TPP)Fe<sup>III</sup>OFe<sup>III</sup>(TPP), 612, 571, 408<sup>14</sup>).

Treatment of **1c** with piperidine in DMF at 55 °C yields a water-soluble tetrapiperidinium salt, (Pipm)<sub>4</sub>H<sub>2</sub>T(*o*-MCbIme)P (**1d**) in which the *meso*-CH<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> Me substituents have been degraded to [-CH<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>Me]<sup>-</sup> moieties (visible spectrum in H<sub>2</sub>O, 655, 597, 562, 527, 424 nm). This degradation reaction is known to remove one of B atoms on either side of the C-C bond in 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>.<sup>15</sup> Since the borons removed are either enantiotopic or diastereotopic, a multitude of isomeric possibilities other than atropisomerism exist for **1d**. A water insoluble Me<sub>4</sub>N<sup>+</sup> salt of the degraded porphyrin is obtained by quantitative metathesis of **1d** with Me<sub>4</sub>NCl. The intensity of the Me<sub>4</sub>N<sup>+</sup> signal (12) relative to the *meso*-CH<sub>2</sub> and  $\beta$ -pyrrole signals (both 2) in the <sup>1</sup>H NMR spectrum of **1e** demonstrates that all four carborane cages have been degraded (the  $\delta$  values in pyridine-*d*<sub>5</sub> are 1.93, 5.5–6.1, and 9.6–9.8, respectively, with the broad multiplet nature of the latter two resonances reasonably attributable to a mixture of isomers (vide supra)).

The intermediacy of  $\alpha,\alpha,\alpha,\alpha$ -*meso*-tetra(*o*-aminophenyl)-porphyrin (**7**)<sup>16</sup> afforded  $\alpha,\alpha,\alpha,\alpha$ -H<sub>2</sub>T(*o*-CbMeAmP)P (**1f**) atropisomerically pure as evidenced by TLC and <sup>1</sup>H NMR. To obtain **1f**, the aminoporphyrin **7** was treated with a 100% excess of the acid chloride 1-ClC(O)CH<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub><sup>17</sup> (**8**) in THF-pyridine at 25 °C followed by hydrolysis of excess **8** and silica gel column chromatography (benzene-ether). The infrared of **1f** (CHCl<sub>3</sub>) shows characteristic  $\nu_{\text{BH}}$  at 2600,  $\nu_{\text{CO(amide)}}$  at 1705,  $\nu_{\text{NH}}$  at 3445, and  $\nu_{\text{CH(carborane)}}$  at 3095 cm<sup>-1</sup>, respectively; the visible spectrum (CHCl<sub>3</sub>) is 418, 512, 543, 572, 652 nm. The <sup>1</sup>H NMR is clean in the  $\beta$ -pyrrole and CH<sub>2</sub> regions unlike those **1b–e** (9.25 (2,  $\beta$ -pyrrole), 8.9 (1, NH), 8.2–7.4 (4, C<sub>6</sub>H<sub>4</sub>), 4.5 (1, CH carborane), and 2.8 (2, CH<sub>2</sub>)).

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## Nature of Naked-Metal-Cluster Polyanions in Solution. Evidence for (Sn<sub>9-x</sub>Pb<sub>x</sub>)<sup>4-</sup> (x = 0–9) and Sn–Sb Clusters

Sir:

Recently, Corbett and his coworkers isolated and determined the crystal structures of several "naked-metal-cluster" polyanions such as Sb<sub>7</sub><sup>3-</sup>, Pb<sub>5</sub><sup>2-</sup>, Te<sub>3</sub><sup>2-</sup>, Sn<sub>5</sub><sup>2-</sup>, Sn<sub>9</sub><sup>4-</sup>, Ge<sub>9</sub><sup>2-</sup>, and Ge<sub>9</sub><sup>4-</sup>.<sup>1</sup> Reversion to the alloy phase from which the clusters are derived was prevented by clever use of the bicyclic 2,2,2-crypt ligand<sup>2</sup> which effectively complexes the alkali metal counterion and thereby precludes electron transfer upon solvent evaporation. Kummer and Diehl<sup>3</sup> have found somewhat more limited success in isolating Sn<sub>9</sub><sup>4-</sup> as a solvate with ethylenediamine. Although these crystallographic investigations have defined the geometries of these interesting clusters in the crystalline state, their nature in solution has been the subject of speculation.<sup>1</sup> We report here *prima facie* evidence for the fluxional nature of the Sn<sub>9</sub><sup>4-</sup> cluster in solution, the existence of (Sn<sub>9-x</sub>Pb<sub>x</sub>)<sup>4-</sup> clusters, and the possibility of SbSn<sub>9</sub><sup>3-</sup> or SbSn<sub>9</sub><sup>1-</sup> cluster.

Alloys of compositions near NaSn<sub>2.25</sub> were dissolved in ethylenediamine (en) to give typical deep-orange-red solutions of Sn<sub>9</sub><sup>4-</sup> which were investigated at both 31.896 and 29.641 MHz by pulse Fourier transform <sup>119</sup>Sn NMR.<sup>4</sup> A sample 85% enriched in <sup>119</sup>Sn was used to locate the position of Sn<sub>9</sub><sup>4-</sup>. A single resonance was found 1230.0 ppm upfield from tetramethyltin (TMT) with very weak satellites due to a <sup>119</sup>Sn–<sup>117</sup>Sn coupling of 254 Hz. Samples prepared from naturally abundant tin gave a 0.046:0.312:1.000:0.312:0.046 quintet compared with calculated intensities of 0.044:0.311:1.000:0.311:0.044.<sup>5</sup> The lines were separated by 127 Hz which gives  $J_{119\text{Sn}-117\text{Sn}} = 254$  Hz. The observation of a single resonance indicates that the individual environments of the static C<sub>4v</sub> structure (monocapped square antiprism)<sup>1a</sup> are averaged<sup>6</sup> in some manner (Figure 1). The observation of <sup>119</sup>Sn–<sup>117</sup>Sn spin-spin coupling shows that the averaging process is intramolecular. Other idealized structures such as the D<sub>3h</sub> tricapped trigonal prism or the C<sub>4v</sub> monocapped cube also have non-equivalent tin environments and would not be expected to show a single resonance with equivalent <sup>119</sup>Sn–<sup>117</sup>Sn couplings.

The magnitude of  $J_{119\text{Sn}-117\text{Sn}}$  is also indicative of a fluxional cluster. The one-bond <sup>119</sup>Sn–<sup>117</sup>Sn coupling constant in a series of hexaorganoditins is known to vary between 4200 and 730 Hz<sup>7</sup> and two-bond Sn–Sn–Sn couplings have been observed to be even smaller than the latter as expected. The 254-Hz coupling for Sn<sub>9</sub><sup>4-</sup> must be a weighted average of one- and two-bond couplings; however, it will be necessary to observe the limiting spectra of nonfluxional Sn<sub>9</sub><sup>4-</sup> before the magnitudes of  $J_{119\text{Sn}-117\text{Sn}}$  and  ${}^2J_{119\text{Sn}-117\text{Sn}}$  are known. We have observed that the spectrum of Sn<sub>9</sub><sup>4-</sup> is the same at –40 °C in NH<sub>3</sub>(*l*) and at 30 °C in ethylenediamine. Corbett has estimated a very low barrier between the C<sub>4v</sub> and D<sub>3h</sub> structures