The Preparation and Characterization of Several *meso*-Tetracarboranylporphyrins

R. C. Haushalter, W. M. Butler, and R. W. Rudolph*

Contribution from the Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109. *Received July 21, 1980*

Abstract: Several *meso*-tetracarboranylporphyrins were prepared and characterized. A Rothemund condensation designed to give a 1,2-$C_2B_{10}H_{11}$ meso substituent (R) was not successful, but with R = 1-CH_2-1,2-$C_2B_{10}H_{11}$ and 1-CH_2-2-CH_3-1,2-$C_2B_{10}H_{10}$, porphyrins were obtained as a mixture of atropisomers. The icosahedral $-C_2B_{10}H_{10}Me$ cages of the latter *meso*-tetracarboranylporphyrins were partially degraded to $[-C_2B_9H_{10}Me]^-$ moieties by piperidine which results in a water-soluble *meso*-tetracarbollylporphyrin. The $\alpha,\alpha,\alpha,\alpha$ atropisomerically pure porphyrin with R = 1-[*o*-C_6H_4-NHC(O)CH_2]-1,2-$C_2B_{10}H_{11}$ was obtained by reaction of $\alpha,\alpha,\alpha,\alpha$-*meso*-tetrakis(*o*-aminophenyl)porphyrin with 1-ClC(O)CH_2-1,2-$C_2B_{10}H_{11}$. The latter amide-linked carboranylporphyrin also was partially degraded to yield a porphyrin with a core and four $[-C_2B_9H_{11}]^-$ metal-binding sites. The free-base porphyrin α^4-$H_2[P(C_6H_4NHCOCH_2C_2B_{10}H_{11})_4]$ gave strikingly dichroic crystals from ethanol/benzene which were assigned the tetragonal space group *P*4/*n* with *a* = 19.513 (11) Å, *b* = 19.506 (8) Å, and *c* = 13.724 (6) Å. A semiquantitative structure was possible with 1324 reflections. Solvent disorder presented problems, but the main geometrical features of the ligand were apparent. Also, ethanol was found hydrogen bonded intramolecularly between the amide substituents, giving a distortion of the protective binding pocket relative to similar porphyrins not containing hydroxylic solvents in the crystal.

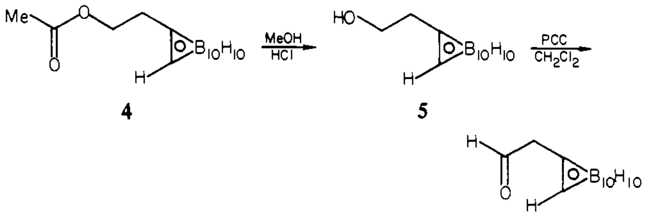
In recent years there have been many examples of synthetic porphyrins and other macrocycles with peripheral substituents designed to modify or protect the metal ion at the core. Many of these complexes were synthesized in connection with hemoglobin model compound studies and include various "tail",[1] "capped",[2] "picket-fence",[3] "crowned",[4] and polymer bound porphyrins. Other porphyrins have substituents that were employed to investigate electron transfer or metal-metal interactions such as the metal complexes of *meso*-tetrakis(nicotinamidophenyl)porphyrins,[5,6] cofacial metalloporphyrinates,[7] and a *meso*-tetraferrocenylporphyrin.[8]

We would like to report the synthesis and some results obtained with a new family of porphyrins, the carboranylporphyrins.[9] The carboranylporphyrins have (2-R-1,2-$C_2B_{10}H_{10}$) icosahedra[10] appended to the meso position of the porphyrin. One of the most attractive features of the carboranylporphyrins is that the carborane cages can be modified in a wide variety of ways which result in large alterations in the physical properties of the porphyrin macrocycle. For instance, it has been possible to prepare, by the partial degradation of the $-C_2B_{10}H_{10}R$ substituents to $-C_2B_9H_{10}R^-$ anions, carboranylporphyrins that span the range from water to chloroform soluble by proper choice of the cage's counterion. Other physical properties that are changed when the cages are degraded include the electronic absorption spectrum and the oxygen affinity of certain metallocarboranylporphyrinates.[9c] In addition, it has been possible to metalate the four $C_2B_9H_{10}R^-$ cages with one type of metal and the porphyrinate core with a second metal to give novel pentametalloporphyrinates.[9c]

Results and Discussion

Synthesis of the Carboranylporphyrins. The carboranylporphyrins were initially conceived as "superstructure" ligands capable of binding several metal atoms per molecule. We hypothesized that it might be possible to observe electron transfer between metal centers either directly, via the porphyrins π system or through bridging ligands. Thus, in principle, it might be possible to coordinate a small molecule to the axial position of the metal in the porphyrinate core and then oxidize or reduce it with redox equivalents from metals bound to the porphyrin's periphery. With these goals in mind, it was desirable to attach the carborane cages as closely as possible to the porphyrin and the synthesis of porphyrin **1**, $H_2[P(C_2B_{10}H_{11})_4]$,[11] was undertaken.

Scheme I



4

5

3

(A) Synthesis of "Methylene-Linked" Carboranylporphyrins, $H_2[P(CH_2C_2B_{10}H_{10}R)_4]$. The synthesis of porphyrin **1** was attempted by the standard Rothemund condensation[12] of pyrrole with carboranylaldehyde **2**, 1-formylcarborane, which was prepared by the ozonolysis of 1-vinylcarborane. Although this condensation was carried out for various lengths of time and also in the presence of several metal salts, no porphyrins were detected in the reaction mixture by TLC or visible spectroscopy. After chromatography, mass spectral and IR analysis, several di- and tripyrrolic carborane-containing fragments were identified in the reaction mixture. The presence of the partial condensation products suggested that the incipient *meso*-$C_2B_{10}H_{11}$ groups were too large to allow the final closure to form the macrocycle. Accurate, space-filling models substantiated this assumption.

If the reaction of **2** and pyrrole failed due to steric hindrance at the incipient meso position, then it seemed that the formation of the macrocycle might be possible if the carborane group were attached to the meso position via a less sterically demanding methylene group. The preparation of 2-carboranylethanal (**3**) was accomplished by the reactions shown in Scheme I. It was

---

(1) Traylor, T. G.; Chang, C. K.; Geibel, J.; Berzinis, A.; Mincey, T.; Cannon, J. *J. Am. Chem. Soc.* **1979**, *101*, 6716 and references therein.

(2) Almog, J.; Baldwin, J. E.; Dyer, R. L.; Peters, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 226.

(3) Collman, J. P.; Gagne, R. R.; Reed, C. A.; Halbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 1427.

(4) Chang, C. K. *J. Am. Chem. Soc.* **1977**, *99*, 2819.

(5) Eliott, M. *J. Chem. Soc., Chem. Commun.* **1978**, 399.

(6) Buckingham, D. A.; Gunter, M. J.; Mander, L. N. *J. Am. Chem. Soc.* **1978**, *100*, 2899.

(7) Chang, C. R. *J. Heterocycl. Chem.* **1977**, *14* (7), 1285-8.

(8) Wollmann, R. G.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 3079.

(9) (a) Haushalter, R. C.; Rudolph, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 4628. (b) *Ibid.*, **1979**, *101*, 7080. (c) Another paper which gives details regarding the metal complexes of the carboranylporphyrinates and oxygenation studies has been submitted for publication.

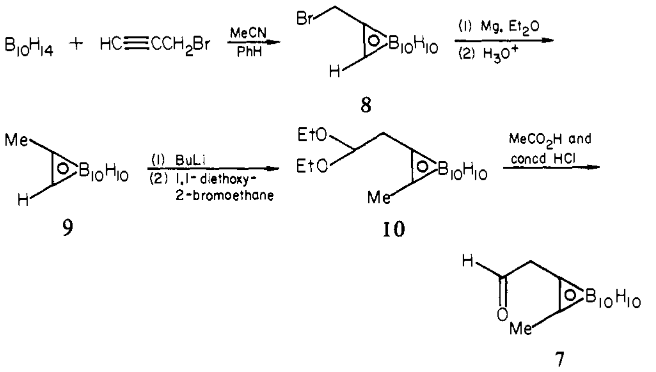
(10) Grimes, R. N. "Carboranes"; Academic Press: New York, 1970.

(11) Abbreviations used: *ar*, atropisomerically random; α^4, porphyrin atropisomer with all substituents on one side of the porphyrin plane; DMF, dimethylformamide; Et, ethyl; Me, methyl; MeIm, 1-methylimidazole; MeOH, methanol; Bu, butyl; OAc, acetate; OEP, octaethylporphyrinate; PCC, pyridinium chlorochromate; THF, tetrahydrofuran; TrIm, 1-(triphenylmethyl)imidazole; TpivPP, tetrakis(pivalimidophenyl)porphyrinate; TPP, *meso*-tetraphenylporphyrinate; PhH, benzene; py, pyridine; pip = piperidine; pipH = piperdinium; P is short for the $C_{20}H_8N_4$ porphyrinate core (exclusive of meso substituents) in most of the formulas.

(12) Adler, A. D.; Longo, F. R.; Finarelli, J. O.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

0002-7863/81/1503-2620$01.25/0

Scheme II



not possible to hydrolyze ester **4** in acidic aqueous solution, but methanolysis proceeded readily[13] to the substituted ethanol **5** in high yield. Oxidation of **5** with pyridinium chlorochromate gave aldehyde **3** in 70% yield after chromatography.[14]

The Rothemund condensation of carboranylaldehyde **3** with pyrrole in refluxing $EtCO_2H$ gave a black reaction mixture which contained the porphyrin chromophore as evidenced by visible spectroscopy. Normally when a Rothemund condensation is carried out the porphyrin precipitates from the cooled propionic acid reaction mixture, but no solid was obtained from the reaction of pyrrole and **3** even after reducing the volume of the solution and chilling. The porphyrin was enriched from the black reaction products by chromatography, and then this crude material was rechromatographed or recrystallized to give an approximately 1% yield of the porphyrin. The dark solid was formulated as $H_2[P(CH_2C_2B_{10}H_{10})_4]$ (**6**) on the basis of visible spectra, elemental analysis, IR, and ^1H and ^{11}B NMR (see Experimental Section). The Cu(II) and Zn(II) complexes of **6** were prepared by treatment of the free-base **6** with $Cu(OAc)\cdot H_2O$ and $ZnCl_2$, respectively, and identified by their visible absorption spectra.

Although the reaction of 2-carboranylethanal and pyrrole allowed the synthesis and identification of the first example of a carboranylporphyrin, the loss of >99% of the expensive boron-starting materials, difficulty in isolation, and the extremely low yields of **6** precluded any serious investigation of the chemistry of this porphyrin.

Since it appeared that the main problem with the synthesis of **6** discussed above was not the formation of the porphyrin but the fact that the porphyrin failed to precipitate from the polar reaction medium and since the somewhat acidic carborane C–H is polar, it seemed possible that replacement of the C–H group in the carborane with a *C*-alkyl group might reduce the solubility in the polar $EtCO_2H$ reaction solvent.

For investigation of this possibility, the synthesis of aldehyde **7**, 2-(2-methylcarboran-1-yl)ethanal, was undertaken. Aldehyde **7** was synthesized by the method shown in Scheme II.

When pyrrole was allowed to react with aldehyde **7** under Rothemund conditions in refluxing $EtCO_2H$ for 5 h, a solid precipitated from the reaction mixture. The visible absorption spectrum and other qualitative tests showed the dark solid to be a free-base porphyrin. Porphyrin **11** was found to be less soluble than **6**, $H_2[P(CH_2C_2B_{10}H_{11})_4]$, in many solvents. It was essentially insoluble in solvents like Et_2O, PhH, or $CHCl_3$, slightly soluble in acetone and quite soluble in DMF or pyridine.

Instead of the 1% yield obtained for porphyrin **6** after lengthy purification procedures, porphyrin **11**, $H_2[P(CH_2C_2B_{10}H_{10}Me)_4]$, was isolated in an essentially pure form in 10–11% yield by simply filtering the cooled reaction mixture.

Porphyrin **11**, pictured in Figure 1, was identified on the basis of the following data. The visible spectrum was that of a typical porphyrin (acetone): 417 (B band), 516, 545, 592, and 664 nm. While it was not possible to obtain conventional electron-impact mass spectra of **11** at temperatures up to >350 °C, the molecular weight was determined by Bernd Soltmann[15] by using the electron-impact-desorption technique[16] at ~450 °C. The mass spectrum showed a base peak corresponding to the parent peak of **11** as part of a manifold of peaks due to the varying ^{10}B:^{11}B ratios in the cages; it was centered at 991 with the cutoff at 998 which corresponded to all 40 boron atoms being ^{11}B. Several members of the parent manifold were peak matched to determine their mass more exactly. For instance, anal. calcd for $^{12}C_{36}{}^{1}H_{70}{}^{10}B_{7}{}^{11}B_{33}{}^{14}N_{4}$: 991.9576. Found: 991.9599. Even at ~450 °C very little fragmentation of **11** was observed in the mass spectrometer with the other prominent peaks, besides the parent, being due mainly to expulsion of the bulky meso substituents.[17] A large manifold was also observed at half the mass of the parent peak with alternating peaks at half-integral mass units and thus was assigned as doubly ionized **11**. The infrared spectrum of the porphyrin was consistent with its formulation with $\nu(BH) = 2555$ cm^{-1} and $\nu(NH) = 3317$ cm^{-1} in addition to vibrations associated with the porphyrin nucleus.[18]

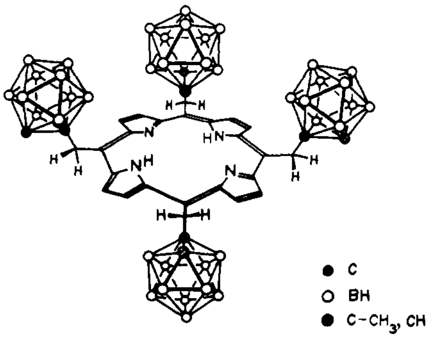


Figure 1. The proposed $\alpha,\alpha,\alpha,\beta$ atropisomer of $H_2[P(CH_2C_2B_{10}H_{10}Me)_4]$ (**11**) and $H_2[P(CH_2C_2B_{10}H_{11})_4]$ (**6**).

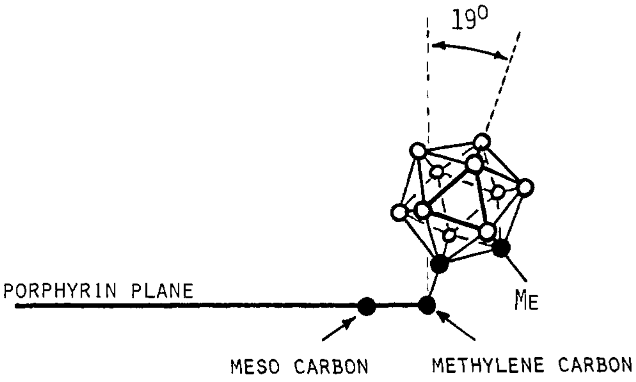


Figure 2. Depiction of preferred geometry of *meso*-CH_2-$C_2B_{10}H_{11}Me$ moiety based on space-filling models.

The proton NMR of **11** revealed several interesting points. On the basis of molecular models it was predicted that there is severely hindered rotation about the meso carbon–cage methylene carbon bond (C_{meso}–$C_{methylene}$). The carboranyl groups are held at approximately 109 – 90 = 19° (see Figure 2) from the normal to the porphyrin plane and strongly interact with the β-pyrrole hydrogens upon rotation about the C_{meso}–$C_{methylene}$ bond. Thus, porphyrin **11** (as well as the aforementioned porphyrin **6**), was expected to exist as a statistical mixture of atropisomers. (Hereafter, porphyrins that are a mixture of atropisomers will be prefixed by the symbol *ar* for atropisomerically random.) The ^1H NMR data for **11** apparently supported the formulation of **11** as a mixture of four atropisomers. When the ^1H NMR

---

(13) Kazanteer, A. V.; Kitorchenko, L. E. *Zh. Obshch. Khim.* **1970**, *40*, 2768.

(14) It was also possible to prepare this compound by the reaction of lithiocarborane and 1,1-diethoxy-2-bromoethane.

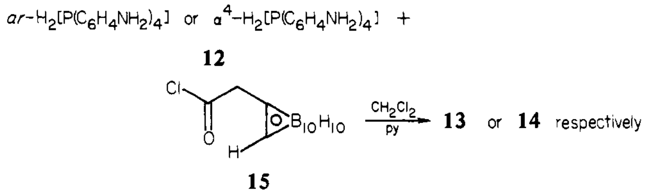
(15) Department of Biochemistry, Michigan State University, East Lansing, MI.

(16) Soltman, B.; Sweely, C. C.; Holland, J. F. *Anal. Chem.* **1977**, *49*, 1165.

(17) The entire $-CH_2C_2B_{10}H_{10}Me$ substituent was expelled.

(18) See J. O. Alben In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979, Vol. III, Chapter 7.

Scheme III



spectrum of **11** was recorded from saturated Me_2SO-d_6 solutions, the signals for the β-pyrrole, meso CH_2 and the cage methyl group all appeared as broad singlets at δ 10.0, 6.3 and 2.9, respectively. However, the spectrum of **11** in pyridine-d_5 solution, in which it is more soluble, showed the three resonances to be multiple presumably due to the various atropisomeric environments.

The N–H region of the ^1H NMR also provided supportive evidence for the existence of the four atropisomers. At 100 MHz, the N–H region showed two signals of slightly different intensity, but at 360 MHz there were three N–H absorptions at −2.26, −2.41, and −2.58 ppm. In addition, the cage methyl region showed four absorptions around 2.8 ppm, and the meso CH_2 group shows multiple absorptions at 360 MHz. It seems reasonable to assign these multiple resonances to the existence of atropisomers that are stable on the NMR time scale. It should be noted that porphyrin **11** was always obtained as an amorphous powder and brief attempts to separate the individual atropisomers by TLC were unsuccessful. In summary, two new "methylene-linked" carboranylporphyrins *ar*-$H_2[P(CH_2C_2B_{10}H_{11})_4]$ (**6**) and *ar*-$H_2[P(CH_2C_2B_{10}H_{10}Me)_4]$ (**11**) have been prepared. The replacement of the hydrogen on C-2 of the carborane cage in **6** with a methyl group in **11** gave a tenfold increase in yield of porphyrin that is easily isolated in pure form.

(B) Synthesis of "Amide-Linked" Carboranylporphyrins, $H_2[P(C_6H_4NHCOCH_2B_{10}H_{10}R)_4]$. In addition to the methylene-linked carboranylporphyrins, another type of carboranylporphyrin linked through an amide group has been prepared by the reaction of carboranyl acid chlorides with *meso*-tetrakis(2-aminophenyl)porphyrin (**12**). In addition to the porphyrins to be discussed here, other examples of porphyrins prepared by this method have been reported[5,6,19] since the original report by Collman and co-workers.[20]

Depending on the final product desired, either the entire atropisomerically random mixture of *ar*-**12** or the $\alpha\alpha\alpha\alpha \equiv \alpha^4$ atropisomer ($\sim C_{4v}$ symmetry), α^4-**12** (i.e., all amino groups on the same side of the porphyrin plane), was subjected to the subsequent acylation reaction. Porphyrin α^4-**12** could be isolated from *ar*-**12** by column chromatography.[20]

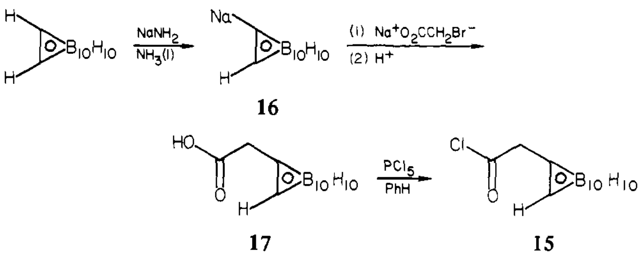
Porphyrins **13**, *ar*-$H_2[P(C_6H_4NHCOCH_2C_2B_{10}H_{11})_4]$, and **14**, α^4-$H_2[P(C_6H_4NHCOCH_2C_2B_{10}H_{11})_4]$, were synthesized (Scheme III) by reaction of excess 2-carboranylacetyl chloride with the tetraaminoporphyrins *ar*-**12** and α^4-**12**, respectively, in CH_2Cl_2 in the presence of pyridine.

The acid chloride **15** was prepared from carborane by the method shown in Scheme IV. The alkylation of sodiocarborane **16** with sodium bromoacetate in liquid ammonia with subsequent acidification provided >90% yield of the 2-carboranylacetic acid **17**. Chlorination of **17** with PCl_5 in benzene gave **15**. The acid chloride **15** could not be prepared by the reaction of **17** with $SOCl_2$.

Porphyrins **13** and **14** were identified by elemental analysis, IR, ^1H and ^{11}B NMR, and visible absorption spectra (see Experimental Section).

Because of the oxygenation experiments and metallocarboranyl-metalloporphyrinate syntheses described in another paper,[9c] it was desirable to delineate the structural nature of the protected pocket formed about the porphyrin core by amide-linked carboranyl substituents and the structure of the α^4-porphyrin was determined.

Scheme IV



Structure. The structure determination for α^4-$H_2[P(C_6H_4NHCOCH_2C_2B_{10}H_{11})_4]$ (**14**) was of a semiquantitative nature. Problems were encountered since a relatively small number of reflections were observed vs. the number of structural parameters to be determined for the large, light atom structure. The measured density also indicated a very large number of solvent molecules were present. These factors, particularly the latter, prevented the precise structure determination of the crystals.

Crystals of **14** were obtained from benzene/EtOH by slow evaporation. Precession photographs showed the crystals to be tetragonal. When removed from the solvent, the crystals were observed to turn to powder presumably due to loss of solvate. The most striking feature of the crystals was their pronounced dichroism. The tetragonal crystals were essentially colorless along the *a* and *b* axes but very dark red along the *c* axis (it will be shown later that the planes of the porphyrins lie parallel to the *ab* plane).

A large crystal with dimensions of 0.25 × 0.48 × 0.47 mm was selected for analysis and rapidly sealed into a capillary with a small amount of the mother liquor. After centering on the diffractometer, the unit cell constants, at room temperature, were found to be a = 19.615 (12) Å, b = 19.616 (8) Å, and c = 13.770 (6) Å. For the data collection, the crystals were cooled to approximately −100 °C whereupon the unit cell parameters shrank to a = 19.513 (11) Å, b = 19.506 (8) Å, and c = 13.724 (6) Å. At the low temperature there were 1324 reflections observed with $I \geq 3\sigma$.

In the tetragonal space groups, the absences $hk0$, $h + k = 2n$ uniquely determine the space group $P4/n$[21] and all calculations were made in this space group.[22]

The initial structure was found by the direct methods program MULTAN 78 which found the asymmetric unit on the fourfold axis at 0, $^1/_2$, z.

After two cycles of isotropic least-squares refinement, a difference map revealed an ethanol molecule which was hydrogen bonded to the N–H of the amide linkage connecting the cage to the phenyl ring of the porphyrin. These additional atoms found in the difference map were placed in the structure, and two subsequent cycles of isotropic and one of anisotropic least-squares refinement gave an R value of 0.25. It should be noted that most of the bond distances in the porphyrin had converged and showed little change during the last two least-squares cycles. A difference map at this stage showed electron density in the unit cell in addition to the ethanols already found hydrogen bonded to each of the amide N–H's. The additional electron density is presumably from additional ethanol molecules at several positions in the unit cell. There appeared to be two ethanol molecules in the "central pocket" created by the bulky carboranylacetamide substituents as well as two ethanol molecules at each corner of the unit cell and two in the center of the unit cell, one above the other on the

---

[19] Gunter, M. J.; Mander, L. N.; McLaughlin, G. M.; Murray, K. S.; Berry, K. J.; Clark, P. E.; Buckingham, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 1470.

[20] Collmann, J. P.; Gagne, R. R.; Reed, C. A.; Walbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 1427.

[21] Refinements in $P4$, $P4$, or $P42_12$ resulted in only diverging structures. It will be shown later that some of the EtOH solvate present cannot conform to $P4/n$ symmetry in an ordered structure.

[22] Summary of crystal data for α^4-$H_2[P(C_6H_4NHCOCH_2C_2B_{10}H_{11})_4]\cdot(EtOH)_x$: space group = $P4/n$; cell dimensions (low temperature) a = 19.513 (11) Å, c = 13.724 (6) Å; volume = 5223 (43) Å^3; mol wt = 1410 + EtOH; Z = 2; d(obsd) = 1.19 g/cm^3, d(calcd) = 1.18 g/cm^3 (for 20 EtOH/unit cell); crystal dimensions = 0.25 × 0.47 × 0.48 mm; radiation = 0.7107 Å; scan range, 2θ = 45°; reflections with $F^2 \geq 3\sigma(F^2)$ = 1324; deviation of standards during collection was ≤5%.

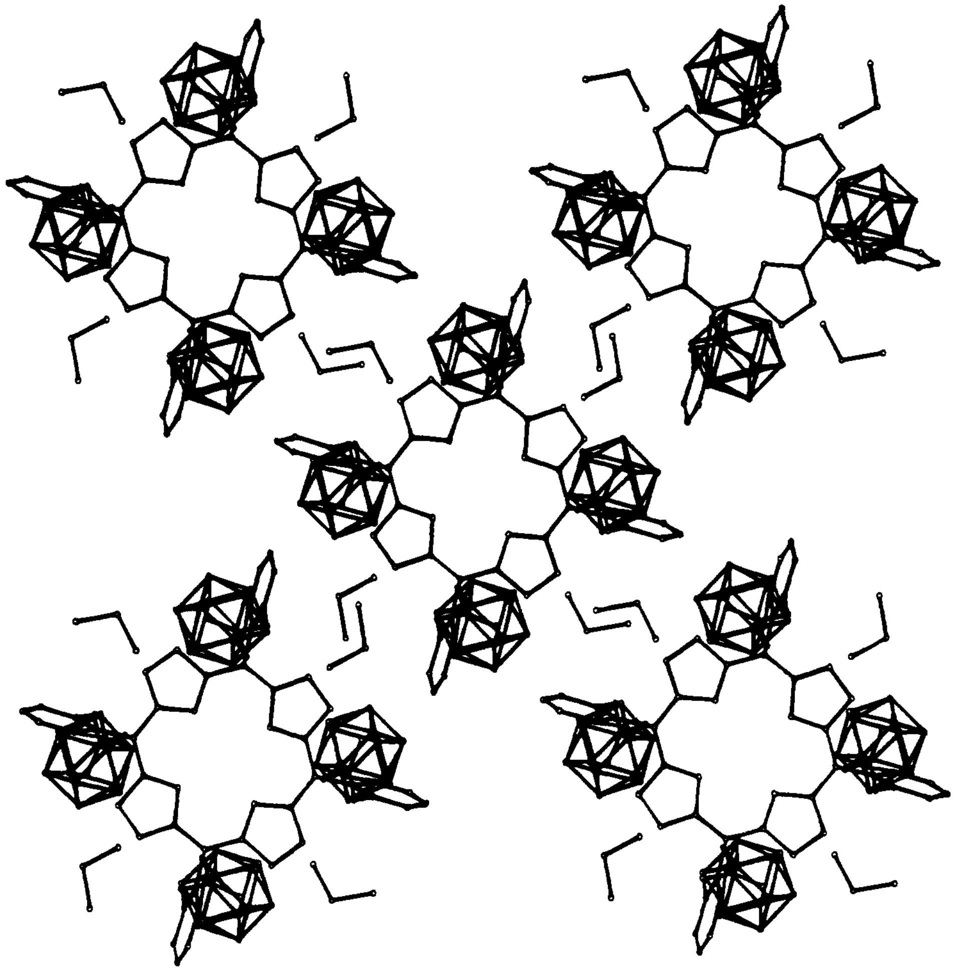


Figure 3. Packing diagram viewed perpendicular to *ab* plane.

$\bar{4}$ axes. Obviously, neither the ethanol molecules in the pocket or those on the $\bar{4}$ axes could conform to the symmetry demanded by *P*4/*n* in an ordered structure. At this stage of the refinement, there appeared to be at least ten molecules of EtOH per porphyrin molecule which means the crystals were about 25% ethanol.

Although subject to possible further refinements with a better model for the distorted solvent and inclusion of the scattering from the hydrogen atoms, the bond distances and angles had converged to reasonable values. In spite of these limitations, the structure determination was still very useful and delineated the cage–porphyrin stereochemical relationships.

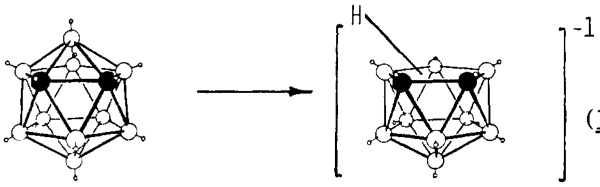
Figure 3 shows the packing in the tetragonal unit cell viewed perpendicular to the *ab* plane. The porphyrin rings are stacked in columns along the *c* axis. Each column of porphyrins is surrounded by four columns composed of enantiomers of the first column. The enantiomers (there are no chiral atoms and the enantiomers are due to packing) are also oriented 180° from each other relative to the *c* axis as shown in Figure 4. A view of one porphyrin molecule is shown in Figure 5.

An interesting feature of the structure was the orientation of the EtOH molecule bonded to each meso substituent as shown in Figure 6 which is a view down the *c* axis. It can be seen that the oxygen of the ethanol solvate is almost exactly equidistant from the nitrogen of one meso substituent and the carbonyl oxygen of the adjacent meso substituent where only the amide moiety is shown for clarity. The distances involved imply moderately strong H bonding is present from the amide NH to the EtOH oxygen as well as from the ethanol OH to the carbonyl oxygen.

Recently, another structure of an α^4-tetrakis(nicotinamidophenyl)porphyrin appeared that was also refined in space group *P*4/*n*.[19] The latter structure also presented difficulty with disorder about the fourfold axis and also had a rather high residual with $R > 0.20$ in spite of several heavy atoms. However, the amide linkages in the structure of *meso*-tetrakis(nicotinamidophenyl)porphyrin also appear to have a skewed appearance similar to the amide linkages of our carboranylporphyrin **14**. This skewness is due to the hydrogen-bonded ethanols in **14**, but the authors of ref 19 do not discuss the possibility of a bridging hydroxylic solvent (H_2O in their case) as found in **14**. Other amide-linked porphyrins whose structures are known appear to have amide groups which are essentially coplanar with the meso phenyls.[23] Although the amide N–H in (1-MeIm)(O_2)Fe(α^4-TpivPP) is directed toward the bound O_2, because of distance, H bonding is not likely.[3] The present case of **14** gives a definitive demonstration that hydroxylic solvents can effect the nature of the pocket in amide-linked picket-fence porphyrins.

To summarize, we have prepared two basic types of carboranylporphyrins, methylene-linked and amide-linked; most of the remaining discussion will deal with the chemistry of these porphyrins.

Scheme V



(18)

Degradation of the Cages. One of the interesting reactions of the $C_2B_{10}H_{12}$ icosahedra is the removal of one boron atom that is adjacent to both carbon atoms by certain bases as shown in Scheme V. The reaction was discovered with hydroxide (alkoxide)

---

(23) Jameson, G. B.; Rodley, G. A.; Robinson, W. T.; Gagne, R. R.; Reed, C. A.; Sorrell, T. N.; Collman, J. P. *Inorg. Chem.* **1978**, *17*, 850, 858.

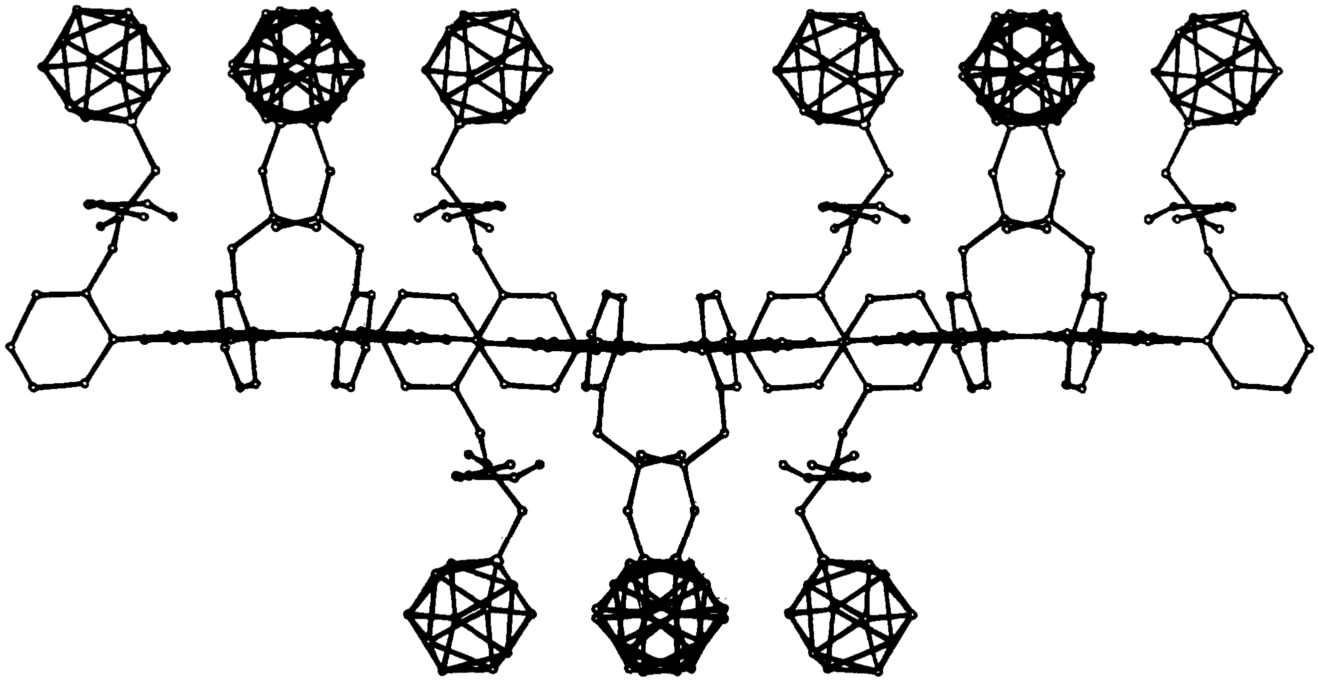


Figure 4. Packing diagram viewed parallel to *ab* plane.

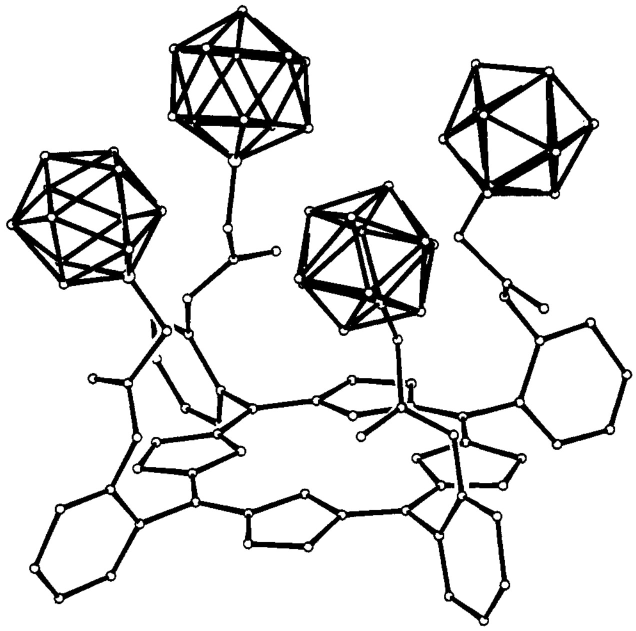


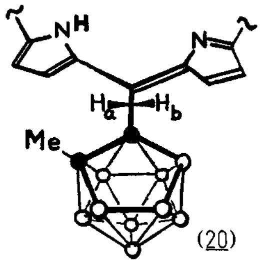
Figure 5. The structure of α^4-$H_2[P(C_6H_4NHCOCH_2C_2H_{10}H_{11})_4]$ (**14**).

as the base[24] but amines such as piperidine allow the reaction to proceed under milder conditions.[25] The product of the piperidine degradation is the piperidinium salt of the dicarbaborate **18**.

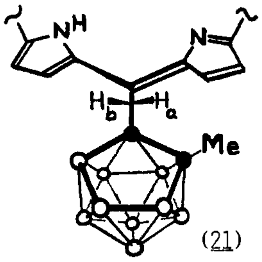
The piperidine method was chosen for the carboranylporphyrin cage degradations because several of the functionalities of the carboranylporphyrins were not stable toward hydroxide ion. Care must also be taken with respect to the sequence of reactions leading to the multimetal porphyrins. For instance, it was not desirable to insert the metal into the porphyrinate core followed by the piperidine degradation of the cages or one would obtain axial ligation of the central metal by the piperidine.[9c]

The cage degradation of *ar*-$H_2[P(CH_2C_2B_{10}H_{10}Me)_4]$ (**11**) was accomplished by the reflux of **11** in 25% piperidine in pyridine for 12–16 h and gave *ar*-$H_2[P(CH_2C_2B_9H_{10}Me{\cdot}pipH)_4]$ (**19**).[26]

The degradation reaction proceeded to completion, as evidenced by (a) the degraded-cage porphyrin being somewhat water soluble unlike the starting material, (b) precipitation when aqueous solutions of **19** were treated with tetraalkylammonium salts (when precipitated with Me_4N^+, integration of the NMe_4^+ ^1H NMR signal relative to that of the β-pyrrole hydrogens showed that degradation was complete), (c) both a shift of the B–H stretching frequency relative to undegraded **11** and the appearance of the piperidinium N–H stretch in the IR spectrum of **19**, (d) the change in the electronic absorption spectrum discussed below, and (e) very convincingly, the observation of two types of meso CH_2 proton in the δ 6.2 region of the ^1H NMR. Structures **20** and **21**



(20)



(21)

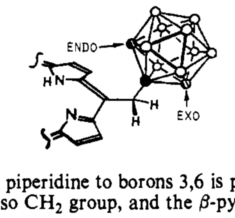
schematically show the two types of hydrogens which do not become equivalent even upon free rotation. Figure 7A shows the

---

(24) Hawthorne, M. F.; Wiesboeck, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 1642.

(25) Zakharkin, L. I.; Kabnin, V. N. *Tetrahedron Lett.* **1965**, 407.

(26) These are more drastic conditions than those required for the piperidine degradation of free carborane which is complete in a few minutes. This difference in reactivity can be rationalized on the basis of the access of the three or six boron atoms to the piperidine. The methyl group attached to the cage probably assumes an exo configuration with respect to the plane of the porphyrin ring.



Thus, the access of the piperidine to borons 3,6 is probably hindered by the porphyrin ring, the meso CH_2 group, and the β-pyrrole hydrogens.

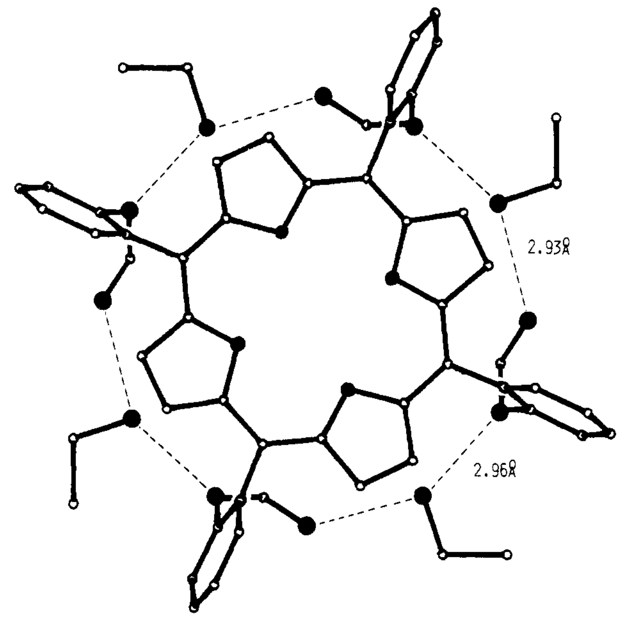


Figure 6. A view of the H-bonded ethanol solvate. The carboranyl moiety is omitted for clarity and the N and O atoms are shaded and enlarged.

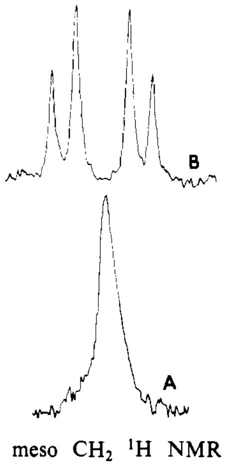


Figure 7. A. The meso CH_2 ^1H NMR signal for *ar*-$H_2[P(CH_2C_2B_{10}H_{10}Me)_4]$ (**11**). B. The corresponding AB pattern in *ar*-$H_2[P(CH_2C_2B_9H_{10}Me\cdot pipH)_4]$ (**19**).

^1H NMR resonance of the CH_2 group in undegraded **11** in Me_2SO-d_6 while Figure 7B shows the CH_2 resonance in degraded **19** with the nonequivalent hydrogens appearing plainly as an AB quartet.

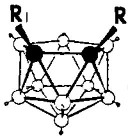
The degradation of amide-linked porphyrins **13** and **14** required less drastic conditions than porphyrin **11**, $H_2[P(CH_2C_2B_{10}H_{10}Me)_4]$. Porphyrin **13** was treated with piperidine in refluxing pyridine for 2 h while **14** was stirred with pyridine–piperidine for 18–24 h at room temperature to give piperidinium salts **22** and **23** as shown in eq 1 and 2. Heating during the

$$\mathbf{13} + \text{pip} \xrightarrow[\text{reflux 2 h}]{\text{py}} \underset{\mathbf{22}}{ar\text{-}H_2[P(C_6H_4NHCOCH_2C_2B_9H_{11}\cdot pipH)_4]} \qquad (1)$$

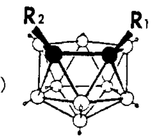
$$\mathbf{14} + \text{pip} \xrightarrow[\text{RT, 18–24 h}]{\text{py}} \underset{\mathbf{23}}{\alpha^4\text{-}H_2[P(C_6H_4NHCOCH_2C_2B_9H_{11}\cdot pipH)_4]} \qquad (2)$$

degradation of **14** was avoided to prevent possible thermal isomerization of the pure α^4-isomer. As was the case with **19**, ^1H NMR showed that the boron elision was quantitative.

It should be noted that the boron atoms 3 and 6 are not equivalent on a 1,2-disubstituted carborane. The compounds obtained by removal of borons 3 and 6 are, in fact, enantiomeric as shown for **24** and **25**. Thus, even for the atropisomerically pure porphyrins a large number of diastereomeric possibilities were obtained from the degradation reaction.



(24)



(25)

The solubility and chromatographic properties of the carboranylporphyrins were greatly altered when the cages were degraded. The piperidinium salts **22** and particularly **23** are very polar and do not dissolve to any appreciable extent in any solvent that is immiscible with water. It was very difficult to pass **23** and its metal complexes through an alumina or a silica column even with acetone or alcohols as eluants.

The cage-degraded tetrapiperidinium porphyrins can be precipitated from aqueous solution by the addition of tetraalkylammonium salts such as tetrabutylammonium which rendered them much more soluble in organic solvents such as $CHCl_3$ and ethyl acetate and made them easier to purify chromatographically. Thus, it is possible to vary the polarity and solubility properties from nonpolar (undegraded cages) to polar and water soluble (degraded cages, piperidinium counterion).

Conclusion

Two linkages were employed successfully to attach carboranyl moieties to the meso positions of the porphyrin core. In both classes (the methylene-linked and the amide-linked carboranylporphyrins) the carborane cages were partially degraded to $[\text{-}C_2B_9H_{10}R]^-$ groups which rendered the porphyrins water soluble and provided four metal-binding sites in addition to that at the porphyrin core. The crystal structure of the free-base α^4-$H_2[P(C_6H_4NHCOCH_2C_2B_{10}H_{11})_4]$ showed ethanol hydrogen bonded intramolecularly between the amide units and a distortion of the protective pocket relative to other similar porphyrins. A variety of metal complexes obtainable from the carboranylporphyrins described here, their O_2-binding propensity, their visible spectra, and some catalytic reactions are described in another paper.[9]

Experimental Section

General Data. All reactions that were suspected of being sensitive to H_2O, O_2, or CO_2 were run either on a vacuum/Schlenk line under deoxygenated (BASF catalyst) N_2 or in an inert atmosphere box (<1 ppm of O_2 or H_2O).

Visible spectra were recorded on a Beckman Model 25 or a Cary 219 UV-visible spectrophotometer. IR spectra were recorded on a Perkin-Elmer 457. ^1H NMR were obtained on a Varian T-60 or T-60A at 60 MHz or a JEOL JNM-PS-100 at 100 MHz or a Bruker WH-360 at 360 MHz. All chemical shifts are reported in δ units from tetramethylsilane ($\delta(Me_4Si) = 0.0$) with δ decreasing for increasing field strength. Microanalyses were performed by either Spang Microanalytical Laboratories or Galbraith Laboratories, Inc. Small amounts of solvents such as Et_2O, C_6H_6, and THF were condensed into the reaction flasks under vacuum from reservoirs of the solvent stored over benzophenone/sodium. Ethanol was distilled from $Mg(OEt)_2$. Other solvents were purified by standard methods. Pyridine, piperidine, and pyrrole were dried over and distilled from KOH or NaOH. All other reagents were obtained commercially and used as received. The BuLi was 2.2 M in hexane.

1-Formylcarborane (2). Vinylcarborane was purchased[27] or synthesized by pyrolysis of 2-carboranylethyl acetate.[28] Vinylcarborane was ozonized by the general method of Pappas[29] et al. Ozone (0.25–0.50 mmol min^{-1} in O_2) was passed through a solution of vinylcarborane **35** in MeOH at −50 to −60 °C until the blue color of the ozone was present. The system was purged with N_2, and then excess dimethyl sulfide was added. The solution was warmed slowly to −10 °C and stirred for 1 h at −10 °C, 1 h at 0 °C, and finally 1 h at room temperature. After evaporation of the excess Me_2S and MeOH, the residue was partitioned between 1:1 Et_2O–petroleum ether and water. The organic layer was

---

(27) Dexsil Corp., Hamden, CT 06514.

(28) Fein, M. M.; Bobinski, J.; Mayes, N.; Schwartz, N.; Cohen, M. S. *Inorg. Chem.* **1963**, *2*, 1111. Heying, T. L.; Ager, J. W.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Symanski, J. W. *Ibid.* **1963**, *2*, 1089.

(29) Pappas, J. J. *Tetrahedron Lett.* **1966**, *36*, 4273.

separated and washed with H_2O (3×), saturated $NaHCO_3$ (1×), and saturated NaCl (2×) and finally dried ($MgSO_4$). The residue was sublimed after evaporation of the solvent to give a nearly quantitative yield of 1-formylcarborane: IR (CS_2) ν(CO) = 1738, ν(BH) = 2580, ν(carborane CH) = 3060, and ν(aldehyde H) = 2840 cm^{-1}; mol wt = 172 (calculated and experimental (mass spectrum)).

2-Carboranylethanal (3). Alcohol **5**, 2-carboranylethanol, was prepared by methanolysis of ester **4**.[30] The alcohol **5** (7.5 g) was added to a slurry of 1.5 equiv of pyridinium chlorochromate in 200 mL of dry, ice-cold CH_2Cl_2 under N_2. The orange mixture turned dark and the ice bath was removed; it was then stirred at room temperature until TLC showed no starting material left. A 1:1 mixture of cyclohexane–Et_2O (250 mL) was added and the solution allowed to stand for 2 h. The brown solution was filtered through celite and evaporated to ~100 mL and applied to a 5 × 20 cm column of silica and eluted with $CHCl_3$. The fractions were monitored by TLC and like eluants combined and evaporated to yield the product: 5.3 g (72%); IR(CS_2) ν(CO) = 1738 and ν(BH) = 2595 cm^{-1}; ^{1}H NMR δ 4.7 (1, carborane C–H), 3.4 (2, CH_2), 9.8 (1, CHO).

1,1-Diethoxy-2-(1-methylcarboran-2-yl)ethane (10). Methylcarborane (15 g) was dissolved in 350 mL of freshly distilled dry benzene under N_2. Next 1.03 equiv of BuLi was added slowly via syringe through a serum cap. The benzene solution was heated to reflux for 5 min and then placed in an ice bath. When the benzene was cold, 15 mL of bromoacetaldehyde diethyl acetal was added over 10 min. After the addition was complete, the solution was warmed to room temperature to give a white precipitate. The solution was stirred overnight and GC analysis (165 °C, 5 ft × $^1/_8$ in. OV-101) showed two peaks, the desired acetal and methylcarborane, in the ratio of 20:1, respectively. Diethyl ether (100 mL) was added and the organic layer washed with water. Workup provided 26 g of a pale yellow oil: ^{1}H NMR δ 1.8 (3, s, cage methyl), 1.0 (6, t, ethoxy methyl), 2.35 (2, d, cage methylene), 3.4 (4, m, ethoxy methylene), 4.5 (1, t, methine); mass spectrum, the parent peak at *m/e* 275 was small compared to peaks at *m/e* 230 corresponding to loss of OEt and *m/e* 201 which was the aldehyde.

2-(1-Methylcarboran-2-yl)ethanal (7). The acetal **10** was dissolved in acetic acid and treated with excess concentrated HCl.[31] The reaction was checked for completeness by neutralization of a small aliquot and GC analysis of the sample. The acetic acid solution was added to several volumes of water and extracted 2× with CH_2Cl_2, and the CH_2Cl_2 extracts were washed with H_2O (3×), saturated $NaHCO_3$ (2×), and saturated NaCl (2×). Drying ($MgSO_4$) and evaporation yielded a thick oil. Addition of an equal volume of heptane caused crystallization to ensue over a few hours. After the mixture was cooled overnight, the white crystals were collected on a chilled frit and rapidly washed with a small amount of cold heptane. The solid was briefly air-dried to yield 65–75% of **7** based on methylcarborane: IR ν(CO) = 1740 cm^{-1}.

2-Carboranylethanoic Acid (17). Carborane (6.0 g) was dissolved in 75 mL of liquid ammonia which contained 1 equiv of $NaNH_2$.[32] After the mixture was stirred for 30 min at −78 °C under N_2, 1 equiv of sodium bromoacetate was added. The ammonia was then allowed to warm to its boiling point and boil away and the residue partitioned between hexane and water with stirring. The water was extracted with two additional portions of hexane. The aqueous phase was then acidified to pH 1 with concentrated HCl to yield a milky white precipitate. The precipitate was extracted into Et_2O which was washed several times with water and then with saturated NaCl and dried ($MgSO_4$). Evaporation of the ether gave 7.3 (87%) of the crude acid which was dried in vacuo. This material was used directly in the preparation of acid chloride **52**.

2-Carboranylethanolyl Chloride (15). The foregoing acid **17** (3.88 g) was added to 85 mL of freshly distilled benzene under N_2. Next 4.00 g of PCl_5 was added rapidly under a nitrogen stream. The solution turned pale yellow, and the solid began to dissolve with evolution of HCl gas. After being stirred at room temperature for 15 min, the solution was refluxed for 30 min. After the mixture was cooled to room temperature, the benzene and $POCl_3$ were stripped. The residue was taken into a N_2-filled glovebag and transferred to a sublimator with a few milliliters of dry Et_2O. The ether was removed under vacuum and the oily residue crystallized in long needles. The residue was sublimed at 80 °C onto a −78 °C cold finger. Removal of the sublimate from the probe in the inert atmosphere box gave 3.76 g (89%) of **15** as a white, crystalline solid: mp 38–39 °C; IR ν(BH) = 2590 and ν(CO) = 1805 cm^{-1}; mass spectrum, small parent at *m/e* 221 but base peaks were parent − ^{35}Cl and parent − ^{37}Cl; ^{1}H NMR δ 4.2 (1, carborane CH), 3.8 (2, methylene).

Attempted Synthesis of $H_2[P(C_2B_{10}H_{11})_4]$ (1). The reaction of equimolar amounts of formylcarborane and pyrrole in refluxing $EtCO_2H$ was tried for varying lengths of time and also in the presence of $ZnCl_2$ and $Cu(OAc)_2 \cdot H_2O$. No porphyrins were detected in any of the reactions.

***ar*-$H_2[P(CH_2C_2B_{10}H_{11})_4]$ (6).** Aldehyde **3** (7.5 g) and pyrrole (2.8 mL) were added to 75 mL of refluxing $EtCO_2H$. After 1 h the solvent was stripped and the residue chromatographed with $CHCl_3$ on a 5 × 40 cm silica column. The porphyrin was easily followed down the column by illuminating with long wavelength UV light. The porphyrinic chloroform eluants were chilled overnight in the refrigerator to yield 87 mg of crude **6**. A sample for analysis was obtained by recrystallization from acetone. IR (KBr) ν(BH) = 2560, ν(CH) (carborane) = 3065, ν(NH) = 3320 cm^{-1}; ^{1}H NMR (100 MHz) (acetone-d_6) δ 9.85 (4, β-pyrrole), 6.36 (4, meso CH_2), 4.8 (2, carborane C–H); −2.7, −2.9 (1, NH) (both the β-pyrrole and CH_2 resonances were multiple as described in the text); visible (acetone) 417, 520, 552, 605 (sh, 595), 665 (sh, 653) nm. Anal. Calcd for $C_{32}H_{60}N_4B_{40}$: C, 41.11; H, 6.64; N, 6.00; B, 46.30. Found: C, 41.17; H, 6.75; N, 6.09; B (by difference, not analysis), 45.99.

***ar*-$H_2[P(CH_2C_2B_{10}H_{10}Me)_4]$ (11).** Aldehyde **7** (5.02 g) and pyrrole (1.8 mL) were refluxed in 200 mL of $EtCO_2H$ for 5 h. The reaction was cooled to room temperature and filtered. The dark powder was washed with MeOH (20 mL), H_2O (20 mL), MeOH (20 mL), and Et_2O (20 mL). The yield was 0.62 g (10% from the aldehyde) of dark purple powder after drying under vacuum at 125 °C until the last traces of $EtCO_2H$ had been removed: ^{1}H NMR (in Me_2SO-d_6) δ 10.0 (4, β-pyrrole), 6.3 (4, meso CH_2), 2.9 (6, carborane methyl), −3.0, −3.15 (1, NH); IR ν(BH) = 2555, ν(NH) = 3317 cm^{-1}; visible (acetone) 417, 519, 550, 592 (sh, 603), 665 (sh, 650) nm. The molecular weight was established as described in the text. Anal. Calcd for $^{12}C_{36}{}^1H_{70}{}^{10}B_7{}^{11}B_{33}{}^{14}N_4$: 991.9576. Found: 991.9599.

***ar*-$H_2[P(C_6H_4NHCOCH_2C_2B_{10}H_{11})_4]$ (13) and α^4-$H_2[P(C_6H_4NHCOCH_2C_2B_{10}H_{11})_4]$ (14).** The procedures for the preparation of these two compounds are similar and any differences are noted. The tetraaminoporphyrin **12** (1.06 g) was dissolved in 125 mL of freshly distilled CH_2Cl_2 under N_2 and 2 mL of dry pyridine added. Acid chloride **15** (1.6 g) was added and the mixture stirred at room temperature for 12 h. Next 20 mL of H_2O was added followed by 50 mL of dilute aqueous ammonia, and the mixture stirred for 2 h (some carboranylacetic acid may be recovered by the subsequent acidification of the aqueous phase). The CH_2Cl_2 solution was washed with dilute NH_3 (2×), H_2O (2×), and saturated NaCl (2×) and dried with $MgSO_4$. The solvent was evaporated to yield 1.9 g (85%) of crude product. Porphyrin **13** was purified at this stage by chromatography on silica (6 cm × 12 cm) with 1:1 CH_2Cl_2–ether while **14** was chromatographed on silica with 1:1:1 acetone–benzene–ether followed by recrystallization from CH_2Cl_2–EtOH or benzene–EtOH. IR ($CHCl_3$) ν(BH) = 2600, ν(CO) (amide) = 1705, ν(NH) (porphyrin) = 3320, ν(NH) (amide) = 3445, and ν(CH) (carborane) = 3095 cm^{-1}; ^{1}H NMR δ 9.25 (2, β-pyrrole), 8.9 (1, NH(amide)), 8.2–7.4 (4, C_6H_4), 4.5 (1, carborane CH), 2.8 (2, CH_2); visible for **13** and **14** (acetone) 418, 512, 543, 572, 652 nm. Anal. Calcd for $C_{60}H_{80}N_8O_4B_{40}$: C, 51.06; H, 5.67; N, 7.94; B, 30.67. Found: C, 51.21; H, 5.81; N, 7.93; B, 30.45.

***ar*-$H_2[P(CH_2C_2B_9H_{10}Me \cdot pipH)_4]$ (19).** Porphyrin **11** was refluxed for 12–16 h in pyridine in the presence of excess piperidine. Typical amounts for degradation were 100 mg of P/25 mL of 25% piperidine in pyridine. The reaction mixture was cooled to room temperature, and the amines were removed on the rotovap. The dark material was stirred with several portions of Et_2O to extract the amines (the porphyrin was insoluble in Et_2O). The residue was taken up in a minimum of acetone and filtered and the light solid (probably $(C_9H_{10}N)_2BH$ or $(C_9H_{10}N)_2BH \cdot pip$) washed with a small amount of acetone. The filtrate was evaporated, redissolved in acetone, and filtered and the filtrate again evaporated. The dark product was again extracted with Et_2O. The residue was then heated at ~120 °C under high vacuum until the vacuum gauge showed no further volatiles (~0.1 Pa) being evolved (usually 2–4 h): ^{1}H NMR (of $(NBu_4)_4$ salt) (acetone-d_6) δ 9.56 (2, β-pyrrole), 5.45 (2, AB quartet, meso CH_2), 2.56 (3, cage methyl), 2.46, 1.13, 0.67 (butyl). IR ν(pipH, NH) = 3180 cm^{-1}; visible (acetone) 421, 527, 562, 597, 655 nm.

***ar*-$H_2[P(C_6H_4NHCOCH_2C_2B_9H_{11} \cdot pipH)_4]$ (13).** The undegraded porphyrin *ar*-**12** was refluxed for 2–4 h in pyridine with excess piperidine. Workup as for **19** gave the degraded porphyrin in essentially quantitative yield: IR ν(NH, pipH) = 3175, ν(BH) = 2500, ν(CO) = 1665 cm^{-1}; ^{1}H NMR (acetone-d_6), essentially the same as the undegraded material except for the broad piperidinium resonances at δ 3.38 and 1.64. The visible spectrum was identical with that of the undegraded material.

α^4-$H_2[P(C_6H_4NHCOCH_2C_2B_9H_{11} \cdot pipH)_4]$ (14). The undegraded porphyrin α^4-**12** was stirred in pyridine with excess piperidine for 24 h under N_2. The solvents were stripped, and the porphyrinic material was

---

(30) Zakharkin, L. I.; Brattsev, V. A.; Stanko, V. I. *Zh. Obshch. Khim.* **1966**, *36*, 886.

(31) Kazantsev, A. V.; Kitovchenko, L. E. *Zh. Obshch. Khim.* **1970**, *40*, 2768.

(32) Stanko, V. I.; Anorova, G. A.; Klimova, T. P. *Zh. Obshch. Khim.* **1966**, *36*, 774.

J. Am. Chem. Soc. **1981**, *103*, 2627–2632 2627

extracted several times with Et_2O. The residue was dissolved in acetone and filtered. The acetone dissolution was repeated and the solution refiltered. The porphyrin was then purified by chromatography on 2-mm silica thick layer plates, eluting with 1:1 acetone–THF. The IR, ^1H NMR, and visible spectra were identical with those of **13**.

Acknowledgment. R.C.H. thanks Allied Chemical Co. and the University of Michigan (A. Knoller and M. Gomberg Fellowships) for partial financial assistance. We thank Bernd Soltman for the EI/D mass spectral determinations. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE 76 23334) for partial support of this research. The National Science Foundation also provided partial support for the purchase of the high-field NMR spectrometer.

Heteroatomic Polyanions of Post-Transition Metals. The Synthesis and Structure of Dithalliumditellurium(2−), $Tl_2Te_2^{2-}$. Skeletal Requirements for Bonding

Robert C. Burns and John D. Corbett*

Contribution from Ames Laboratory—DOE[1] *and the Department of Chemistry, Iowa State University, Ames, Iowa 50011.* *Received October 6, 1980*

Abstract: Reaction of the alloy composition KTlTe with 2,2,2-crypt in ethylenediamine (en) produces a red-brown solution from which dark brown crystals of $(2,2,2\text{-crypt-K}^+)_2Tl_2Te_2^{2-}\cdot$en are precipitated by addition of ethylamine. The composition and structure of the crystals were established by single-crystal X-ray diffraction employing 4144 independent reflections ($I > 3\sigma(I)$) collected on an automated diffractometer at room temperature by using monochromatized Mo Kα radiation. The compound crystallizes in space group $P\bar{1}$, a = 12.867 (4) Å, b = 20.957 (3) Å, c = 11.191 (3) Å, α = 90.71 (2)°, β = 112.63 (2)°, γ = 93.24 (2)°, V = 2779 (1) Å^3, and Z = 2. The structure was solved by Patterson and Fourier methods, and positional and thermal parameters of the 62 nonhydrogen atoms were refined to final agreement indices of R = 0.097 and R_w = 0.114. The $Tl_2Te_2^{2-}$ ring has a butterfly shape with the thallium atoms in the fold, a dihedral angle of 49.9°, and Tl–Te distances between 2.929 (3) and 2.984 (2) Å. The last are deduced to be reasonable single-bond separations while the cross-ring distances of 3.600 (3) and 4.414 (3) Å for Tl–Tl and Te–Te, respectively, are plausible nonbonding separations. The anion configuration is considered to derive from a square-planar geometry (D_{2h}) as a consequence of Te–Te nonbonding repulsions, which leads to the diamond shape, and a fold at the thallium atoms because of predominance of p-orbital bonding for that element, yielding internal angles of about 97° and 75° at Tl and Te, respectively. The low stability evident for homopolyatomic species of the heavy post-transition elements in anions of elements to the left of Sn and Pb and in cations for elements before Sb and Bi appears related to skeletal bonding requirements. All known examples, including the polyborane(2−) anions, contain a minimum of somewhat over two p electrons per atom. The use of mixed elements involving one which is more electron-rich accordingly allows the formation of polyatomic anions for the electron poorer elements such as $Tl_2Te_2^{2-}$ for thallium.

In a series of papers reported almost 50 years ago, Zintl and co-workers[2-5] described their extensive electrochemical studies on solutions of sodium metal alloys of many post-transition elements in liquid ammonia. Numerous homopolyatomic anionic species such as Pb_9^{4-}, Sn_9^{4-}, Pb_7^{4-}, Sb_7^{3-}, Bi_5^{3-}, Te_4^{2-}, and Sb_3^{3-} were identified from these investigations in conjunction with the results of exhaustive alloy extractions with the same solvent. However, attempted isolation of the indicated species by evaporation of the ammonia resulted in either amorphous products or normal intermetallic phases, probably because of the greater electron delocalization in, and hence stability of, the metallic phases.

Recently, a general route to the stabilization of some of the above as well as other polyatomic anions has been developed in which the bicyclic 2,2,2-crypt ligand is used to complex the alkali metal cation (Na^+ or K^+) and to prevent electron transfer back from the anion to the cation in the solid state. So far, salts containing the polyatomic anions, Sn_9^{4-},[6] Ge_9^{4-} and Ge_9^{2-},[7] Pb_5^{2-} and Sn_5^{2-},[8] Sb_7^{3-},[9] Bi_4^{2-},[10] and Te_3^{2-}[11] have been isolated from ethylenediamine (en) solution and structurally characterized in these laboratories. In addition, the As_{11}^{3-} anion has recently been so synthesized and structurally characterized by Belin.[12] The anionic species Pb_9^{4-} and Sn_9^{4-} have also been identified by Rudolph and co-workers[13] in liquid NH_3 and en solution by using ^{119}Sn and ^{207}Pb NMR, and mixed-metal M_9^{4-} ions containing both tin and lead were seen as well. Other species containing both tin and antimony were also observed in these NMR studies, although in no case was a solid phase containing the potential heteropolyatomic species isolated. Simultaneously, mixed-metal systems utilizing crypt have been under investigation in these laboratories, seeking to stabilize solids containing heavy elements from the earlier post-transition groups, e.g., mercury and thallium. Zintl and co-workers were not able to obtain any evidence in their studies for homoatomic anions of groups 2 or 3 (i.e., Zn, Cd, Hg, In, and Tl) in ammonia solution,[2] and addition of crypt has in most cases not given significantly better results. The use of mixed heavy

---

* To whom correspondence should be addressed at Ames Laboratory—DOE.

(1) Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Assistant Secretary for Energy Research, Office of Basic Energy Sciences, WPAS-KC-02-03.

(2) Zintl, E.; Goubeau, J.; Dullenkopf, W. *Z. Phys. Chem., Abt. A.* **1931**, *154*, 1–46.

(3) Zintl, E.; Harder, A. *Z. Phys. Chem., Abt. A* **1931**, *154*, 47–91.

(4) Zintl, E.; Dullenkopf, W. *Z. Phys. Chem., Abt. B* **1932**, *16*, 183–194.

(5) Zintl, E.; Kaiser, H. *Z. Anorg. Allg. Chem.* **1933**, *211*, 113–131.

(6) Corbett, J. D.; Edwards, P. *J. Am. Chem. Soc.* **1977**, *99*, 3313–3317.

(7) Belin, C. H. E.; Corbett, J. D.; Cisar, A. *J. Am. Chem. Soc.* **1977**, *99*, 7163–7169.

(8) Edwards, P.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 903–907.

(9) Adolphson, D. G.; Corbett, J. D.; Merryman, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 7234–7239.

(10) Cisar, A.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 2482–2487.

(11) Cisar, A.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 632–635.

(12) Belin, C. H. E. *J. Am. Chem. Soc.* **1980**, *102*, 6036–6040.

(13) Rudolph, R.; Wilson, W. L.; Parker, F.; Taylor, R. C.; Young, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 4269.

0002-7863/81/1503-2627$01.25/0