J. Am. Chem. Soc. 2001, 123, 9447−9448 9447

Synthesis of the First Corrolazine: A New Member of the Porphyrinoid Family

Bobby Ramdhanie,[†] Charlotte L. Stern,[‡] and
David P. Goldberg*[,†]

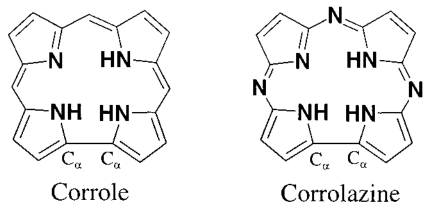
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218
X-ray Crystallography Facility, Northwestern University
Evanston, Illinois 60208

Received May 18, 2001

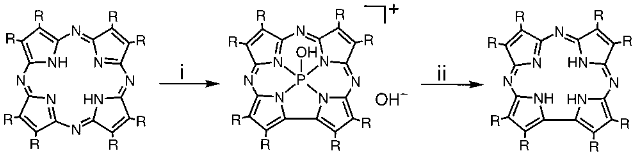
There has been great interest in the synthesis of new porphyrinoid compounds, including expanded and contracted porphyrins and their related tetrapyrrolic isomers.[1] Recently, a surge of activity has occurred concerning a class of porphyrinoid compounds known as corroles.[1−4] The basic corrole framework is distinguished from that of porphyrins by a direct C$_\alpha$−C$_\alpha$ linkage (Chart 1). These macrocycles exhibit some spectacular properties that differ dramatically from their porphyrin counterparts; perhaps the most striking property is their ability to stabilize high-valent oxidation states, for example, Fe(IV),[5] Co(V),[6] and even Mn(V)[7] corroles are thermally stable. This stability must be due, at least in part, to the trianionic charge of the fully deprotonated macrocycle. The analogous, yet highly elusive, metalloporphyrin species are postulated as active intermediates in numerous mechanisms involving metalloporphyrin catalysis[8] and heme protein reactivity.[9] Thus, corroles are attractive systems to study not only for their fundamental physicochemical properties but also for their applications in catalysis[10] and their relevance to the mechanism of action of heme proteins. Corrole syntheses typically have involved difficult multistep methods which have prohibited their routine use, especially by those workers uninitiated in the methods of preparing porphyrinoid isomers.[1] Recently, more practical synthetic methods have begun to emerge.[11] We describe here the facile synthesis of the first triazacorroles from a porphyrazine (Pz, tetraazaporphyrin) precursor, which form a new class of porphyrinoid compounds that we have given the trivial name *corrolazine* (Cz) (Chart 1).

Porphyrazines are relatively easy to prepare, and their electronic, steric, and solubility properties can be tuned over a wide range by incorporating a variety of different peripheral substituents.[12,13] We speculated that the Pz system would make a versatile and accessible synthon to a new family of corrole-type macrocycles in which the *meso* carbon atoms have been replaced by nitrogen atoms but the aromatic corrole framework and 3$^-$ charge would be retained. The synthesis of the phosphorus corrolazine [(TBP)$_8$CzP(OH)]OH (TBP = 4-*tert*-butylphenyl) (**1**), was accomplished via the ring contraction of a porphyrazine precursor, as shown in Scheme 1. Similar methods utilizing a phthalocyanine precursor had led to the formation of the related triazatetrabenzcorrole (TBC) ring, although the metal-free TBC compound could not be prepared.[14−16] It is important to obtain the metal-free form of a new porphyrinoid ring system, since it is this form which provides easy access to transition metal derivatives via simple metal insertion. We have synthesized the metal-free corrolazine, (TBP)$_8$CzPzH$_3$ (**2**), through a novel reductive demetalation strategy.

Chart 1



Scheme 1[a]



[a] Reagents and conditions: (i) a: 35 equiv of PBr$_3$, pyridine, 115 °C, 24 h; b: additional 35 equiv of PBr$_3$, 24 h (ii) 37 equiv of Na, NH$_3$/THF, −78 °C, 20 min.

Treatment of the porphyrazine (TBP)$_8$PzH$_2$, which was easily prepared on a 1−3 g scale following modified literature procedures,[17] with excess PBr$_3$ in pyridine followed by quenching with MeOH gives **1** as a lustrous green solid in 58% yield (0.5 g) after purification by column chromatography (silica gel, CH$_2$Cl$_2$:MeOH 99:1 v/v eluent). The phosphorus porphyrazine (TBP)$_8$-PzP(OMe)$_2$ (yield $< 2\%$) (**3**) is also formed as a side-product during this reaction. The ^{1}H NMR spectrum of **1** in CDCl$_3$ displays four distinct *tert*-butyl resonances and a well-resolved pattern of AB doublets in the aromatic region that are expected for the C_{2v} symmetry of the corrolazine structure. The data from ^{13}C NMR spectroscopy, FAB-MS and elemental analysis are all consistent with the identity of **1**. The UV−vis spectrum of **1** shows intense peaks in the Soret (451 nm ($\epsilon = 13.7 \times 10^4$)) and Q (535, 552, 591, 641 ($\epsilon = 8.0 \times 10^4$) nm) band regions due to $\pi-\pi^*$ transitions that are expected for a fully aromatic 18π-electron ring system.

The ^{31}P NMR spectrum of **1** in CDCl$_3$ reveals a single peak at −111.2 ppm (relative to external H$_3$PO$_4$), which is quite similar

---

[†] The Johns Hopkins University.

[‡] Northwestern University.

(1) Sessler, J. L.; Weghorn, S. J. *Expanded, Contracted, & Isomeric Porphyrins*; Elsevier Science Inc.: New York, 1997.

(2) (a) Paolesse, R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M. and Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 2, pp 201−232. (b) Erben, C.; Will, S.; Kadish, K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 2, pp 233−300.

(3) For the first major theoretical study on corroles, see: Ghosh, A.; Wondimagegn, T.; Parusel, A. B. J. *J. Am. Chem. Soc.* **2000**, *122*, 5100−5104.

(4) Licoccia, S.; Paolesse, R. *Struct. Bonding* **1995**, *84*, 71−133.

(5) Vogel, E.; Will, S.; Tilling, A. S.; Neumann, L.; Lex, J.; Bill, E.; Trautwein, A. X.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 731−735.

(6) Will, S.; Lex, J.; Vogel, E.; Adamian, V. A.; Van Caemelbecke, E.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 5577−5583.

(7) Gross, Z.; Golubkov, G.; Simkhovich, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 4045−4047.

(8) See for example: Groves, J. T.; Gross, Z.; Stern, M. K. *Inorg. Chem.* **1994**, *33*, 5065−5072 and references therein.

(9) (a) Sono, M.; Roach, M. P.; Coulter, E. D.; Dawson, J. H. *Chem. Rev.* **1996**, *96*, 2841−2887. (b) Ator, M. A.; Ortiz de Montellano, P. R. In *The Enzymes*; Sigman, D. S., Boyer, P. D., Eds.; Academic Press: New York, 1990; Vol. XIX, p 214.

(10) Gross, Z.; Simkhovich, L.; Galili, N. *J. Chem. Soc., Chem. Commun.* **1999**, 599−600.

(11) (a) Gross, Z.; Galili, N.; Simkhovich, L.; Saltsman, I.; Boshansky, M.; Bläser, D.; Boese, R.; Goldberg, I. *Org. Lett.* **1999**, *1*, 599−602. (b) Paolesse, R.; Jaquinod, L.; Nurco, D. J.; Mini, S.; Sagone, F.; Boschi, T.; Smith, K. M. *J. Chem. Soc., Chem. Commun.* **1999**, 1307−1308. (c) Gryko, D. T. *J. Chem. Soc., Chem. Commun.* **2000**, 2243−2244.

(12) Michel, S. L. J.; Hoffman, B. M.; Baum, S. M.; Barrett, A. G. M. *Prog. Inorg. Chem.* **2001**, *50*, 473−596.

(13) Kobayashi, N. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 2, pp 301−360.

(14) Li, J.; Subramanian, L. R.; Hanack, M. *Eur. J. Org. Chem.* **1998**, 2759−2767.

(15) Li, J.; Subramanian, L. R.; Hanack, M. *J. Chem. Soc., Chem. Commun.* **1997**, 679−680.

(16) Fujiki, M.; Tabei, H.; Isa, K. *J. Am. Chem. Soc.* **1986**, *108*, 1532−1536.

(17) Nie, H.; Barrett, A. G. M.; Hoffman, B. M. *J. Org. Chem.* **1999**, *64*, 6791−6796.

10.1021/ja011229x CCC: $20.00

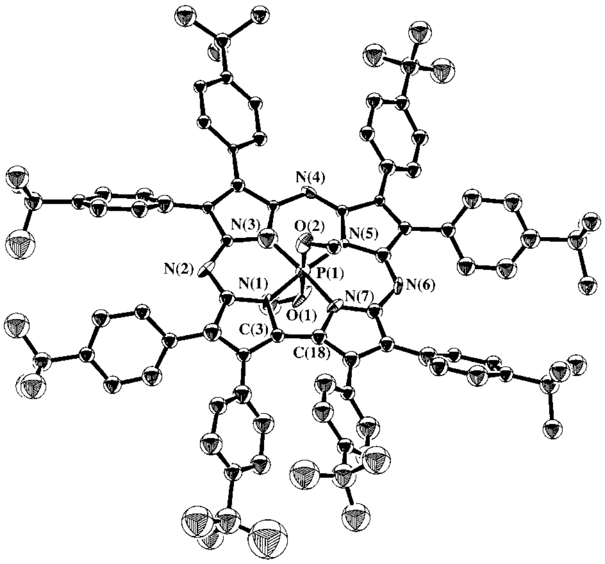


Figure 1. Molecular structure of [$(TBP)_8CzP(OMe)_2$] (**1a**). Hydrogen atoms have been omitted for clarity.

to the five-coordinate phosphorus signal of $\delta = -102.5$ ppm for [(EMC)P(OH)]Cl,[18] the only crystallographically characterized phosphorus corrole reported to date until this work. In comparison, six-coordinate phosphorus porphyrins typically fall within the range $-180 < \delta$ (^{31}P) < -230 ppm.[19] In addition, the ^{31}P NMR spectrum of six-coordinate $(TBP)_8CzP(OMe)_2$ (**1a**), which is isolated after recrystallization of **1** from CH_2Cl_2/MeOH as described below, reveals a typical six-coordinate phosphorus signal at $\delta = -192.1$ ppm (see Supporting Information). From the ^{31}P NMR data we conclude that the solution structure of **1** contains a five-coordinate phosphorus atom with one axial ligand.[20]

Recrystallization of [$(TBP)_8CzP(OH)$]OH from MeOH/CH_2Cl_2 led to the structure[21] of **1a** shown in Figure 1. The expected corrole linkage between the C_α carbon atoms (C(3)−C(18) = 1.42(2) Å) is clearly evident. Interestingly, the X-ray structure reveals that the axial hydroxide ligand has been replaced by two methoxide ligands which likely come from the solvent of crystallization, (P−O(1) = 1.72(2) Å; P−O(2) = 1.69(1) Å), resulting in a six-coordinate P(V) ion in the crystal structure. The corrolazine nucleus is nearly planar, with an average deviation of 0.065 Å for the mean plane of the 23 atom macrocyclic core. The phosphorus atom sits almost directly in this plane (P−Cz(plane) = 0.034 Å). The P−N distances ($P-N_{av} = 1.77$ Å) are similar to those found for $[(EMC)P(OH)]^+$ ($P-N_{av} = 1.80$ Å),[18] and the core sizes of these compounds are unexpectedly the same (corrolazine: $N_{pyrrole}-N_{pyrrole}$(trans) = 3.54 Å; $[(EMC)P(OH)]^+$: 3.51 Å). In comparison, the analogous $N_{pyrrole}-N_{pyrrole}$(trans) distance of a porphyrazine is typically smaller than that of a porphyrin.[22] In contrast to the structural trend observed for conventional metallocorrolates,[23] the two shortest P−N bonds do not involve the nitrogen atoms adjacent to the $C_\alpha-C_\alpha$ linkage.

Given the importance of the fundamental redox properties of corroles, we have examined the electrochemical behavior of **1**. A cyclic voltammogram of **1** in CH_2Cl_2 (see Supporting Information) reveals two reversible reductions centered at −0.80 and −1.33 V, and a single irreversible oxidation at 1.16 V.[24] The potential difference between the first reduction and oxidation waves is $\Delta E_{1/2} = 1.96$ V, which is similar to the $\Delta E_{1/2}$ value for phosphorus corroles[25] and many metalloporphyrins ($\Delta E_{1/2} = 2.25 \pm 0.15$ V),[26] and closely matches that found for certain alkyl-substituted porphyrazines ($\Delta E_{1/2} = 2.14$ V).[13] This value has been associated with the so-called electrochemical HOMO−LUMO gap,[25] and although for **1** this assignment is preliminary, it may imply that the frontier orbitals of the corrolazine are similar to that of other porphyrinoid compounds. The process centered at $E_{1/2} = -1.33$ V is tentatively assigned as a reduction of the phosphorus atom. These results suggested to us that the phosphorus could be removed by *chemical reduction*.

Attempts to demetalate **1** with strong acids such as TFA, H_2SO_4, HNO_3, and H_3PO_4 failed to yield the phosphorus-free product **2**. In light of the cyclic voltammetry data for **1**, we anticipated that the phosphorus(V) ion could be reduced without destruction of the ring, inducing a concomitant expansion in its ionic radius that would force it out of the central cavity and favor formation of the metal-free compound.[27] Indeed, the reduction of **1** with Na/NH_3/THF afforded the metal-free corrolazine **2** in 52% yield (0.05 g) after column chromatography (silica gel, CH_2Cl_2:hexanes 60:40 v/v eluent). Direct evidence for the $N_{pyrrole}-H$ bonds comes from FTIR spectroscopy; a sharp band for the N−H stretch is observed at 3361 cm^{-1} (KBr pellet), which is close to those reported for metal-free porphyrins[28] and porphyrazines.[13] The absorption spectrum of **2** in pyridine exhibits Soret (467 nm ($\epsilon = 1.9 \times 10^4$)) and Q (668 nm ($\epsilon = 1.1 \times 10^4$)) bands that are red-shifted as compared to the phosphorus compound, but provides evidence that the aromaticity of the ring is still intact.

The facile syntheses of compounds **1** and **2** should be compatible with a variety of peripheral substituents, which will allow for the preparation of a new family of corrole-type compounds with adjustable steric and electronic properties. The metal-free Cz should provide access to a wealth of new transition metal corrole chemistry. Studies with a number of first-row transition metals are already underway.

Acknowledgment. This work was generously supported by the NSF (Career Award CHE-0094095 to D.P.G and CRAEMS CHE-0089168) and the ACS-PRF (34413-G3 to D.P.G.). B.R. is grateful for an Alexander Kossiakoff Fellowship.

Supporting Information Available: Synthetic characterization data for **1**−**3**, **1a** and the cyclic voltammogram of **1** (PDF). X-ray data in CIF format for **1a**·$2CH_2Cl_2$·$0.75H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

JA011229X

---

[18] H_3EMC = 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole. Paolesse, R.; Boschi, T.; Licoccia, S.; Khoury, R. G.; Smith, K. M. *J. Chem. Soc., Chem. Commun.* **1998**, 1119−1120.

[19] Barbour, T.; Belcher, W. J.; Brothers, P. J.; Rickard, C. E. F.; Ware, D. C. *Inorg. Chem.* **1992**, *31*, 746−754.

[20] The possibility that both OH^- species are coordinated to the P atom in the *solid state* cannot be ruled out. For precedent concerning OH^- as a free counterion for P(V) porphyrins, see: (a) Rao, T. A.; Maiya, B. G. *Inorg. Chem.*, **1996**, *35*, 4829−4836. (b) Mongani, S.; Meyer, F., Cullen, D. L.; Tsutsui, M.; Carrano, C. J. *Inorg. Chem.*, **1983**, *22*, 400−404.

[21] Crystallographic data for **1a**·$2CH_2Cl_2$·$0.75H_2O$: Monoclinic, space group $P2_1/c$, a = 15.852(4) Å, b = 23.245(5) Å, c = 25.777(6) Å, β = 104.835(4)°, V = 9181.5(33) Å^3, Z = 4, μ = 1.99 cm^{-1}, T = −120 °C, 84779 reflections, 22535 independent reflections (R_{int} = 0.206); $R1$ = 0.125, and $wR2$ = 0.176. The low quality of the structure is due to weak crystal diffraction, but the connectivity of **1a** is not in doubt.

[22] Vangberg, T.; Ghosh, A. *J. Am. Chem. Soc.* **1999**, *121*, 12154−12160.

[23] Paolesse, R.; Licoccia, S.; Bandoli, G.; Dolmella, A.; Boschi, T. *Inorg. Chem.* **1994**, *33*, 1171−1176.

[24] All potentials are referenced versus Ag/AgCl. Electrolyte, 0.1 M Bu_4NPF_6; glassy carbon working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode.

[25] Kadish, K. M.; Erben, C.; Ou, Z.; Adamian, V. A.; Will, S.; Vogel, E. *Inorg. Chem.* **2000**, *39*, 3312−3319.

[26] Kadish, K. M. *Prog. Inorg. Chem.* **1986**, *34*, 435−605.

[27] Marrese, C. A.; Carrano, C. J. *Inorg. Chem.* **1983**, *22*, 1858−1862.

[28] Mason, S. F. *J. Chem. Soc.* **1958**, 976−982.