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Octalkoxy-Substituted Phosphorus(V) Triazatetrabenzcorroles via Ring Contraction of Phthalocyanine Precursors

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As part of efforts toward developing the synthesis of novel corrole analogues, the new triazatetrabenzcorrole (TBC) phosphorus(V) compounds $(BuO)_8(TBC)P(OCH_3)_2$ (**3**), $[(BuO)_8(TBC)P(OH)]^+OH^-$ (**4**) ($(BuO)_8TBC$ = 3,6,10,13,17,20,24,27-octabutoxytriazatetrabenzcorrolate), and $[(BuO)_8Cl_8(TBC)P(OH)]^+OH^-$ (**7**) ($(BuO)_8Cl_8TBC$ = 3,6,10,13,17,20,24,27-octabutoxy-4,5,11,12,18,19,25,26-octachlorotriazatetrabenzcorrolate) were prepared. These TBCs were synthesized via a ring-contraction reaction mediated by PBr_3 in pyridine in which a *meso*-nitrogen atom is extruded from an appropriate phthalocyanine precursor. Two of the compounds prepared, **3** and **4**, are contracted analogues of the parent phthalocyanine $(BuO_8)PcH_2$ (**1**) 1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine, which has been shown for the first time to be susceptible to ring-contraction despite the potential steric crowding imposed by the butoxy substituents. Likewise, the octachloro-substituted $(BuO_8)Cl_8PcH_2$ (**6**), 1,4,8,11,15,18,22,25-octabutoxy-2,3,9,10,16,17,23,24-octachlorophthalocyanine, has also been shown to smoothly afford **7** via the same ring-contraction method. In addition, a rare example of a bona fide phosphorus(V) phthalocyanine, $[(BuO)_8(Pc)P(OCH_3)_2]^+OH^-$ (**2**), has been prepared for spectroscopic comparisons with the TBC compounds. These molecules are all extremely soluble in common organic solvents because of the octabutoxy substituents and have been characterized in detail by ^{1}H NMR, ^{31}P NMR, UV–vis, MALDI-MS, elemental analysis, and electrochemical studies. A clear trend in the phosphorus chemical shifts for 5 versus 6 coordination has been delineated: ^{31}P NMR for **2**, −179.8; **3**, −186.1; **4**, −105.1; and **7**, −105.1. These data are compared to the ^{31}P chemical shifts for related porphyrinoid(P(V)) molecules. The MALDI-MS data reveal the tendency of the TBC macrocycles to ionize as the radical cations ($M^{+\bullet}$) and has been useful in determining the axial ligands at phosphorus. A consequence of ring-contraction is reflected in the dramatic red-shifts (∼200 nm) observed for the Soret bands of the TBC compounds relative to the parent phthalocyanines. The magnitude of the red-shift is much greater than that reported for other TBCs. In addition, insertion of phosphorus causes a large red-shift in the Q-band of **2** found at 889 nm compared to 760 nm for **1**. Cyclic voltammetry of the compounds in this study reveals multiple oxidation and reduction waves for each compound, and some interesting trends in redox potentials have been observed. The CV data for the octachloro-substituted compounds **6** and **7** show that the Cl substituents have an expected strong electron-withdrawing effect on the macrocycles. In general, the TBC compounds are significantly easier to oxidize and harder to reduce than the Pc counterparts, supporting the notion that corrole-type macrocycles favor higher oxidation states.

Introduction

The synthesis of isomeric, expanded and contracted analogues of porphyrins has emerged as an active and diverse area of research in the last several years.[1] Of the many interesting compounds generated in this area, the contracted analogues known as corroles have received much attention as of late.[2−5] Corroles are contracted porphyrins in that they are missing one *meso*-carbon atom but still retain the aromatic, tetrapyrrolic structure of the basic porphyrin ring. As early as 1965, Johnson and Kay discussed corroles in the literature as part of their investigations into the chemistry

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of cobalamin.[6] However, the initial synthetic routes used to form corroles were quite laborious and low-yielding, and thus research on these macrocycles lagged behind the investigation of other compounds such as porphyrins and phthalocyanines for many years. Recent advances in the syntheses of corroles, and in particular the *meso*-aryl-substituted corroles, has begun to rectify this situation.[7−11] However, corrole analogues, apart from the tris(*meso*-aryl) derivatives, remain relatively difficult to prepare.

We have recently discovered a facile method for the synthesis of a triazacorrole, an analogue of corrole in which the three *meso*-carbon atoms have been replaced by nitrogen atoms.[12−14] We have demonstrated that the triazacorrole (or "corrolazine") ring has the ability to stabilize high oxidation states at the central metal ion, which is one of the more fascinating properties of corrole ligands.[12,15] At the same time, we have been interested in the development of the related phthalocyanine-corrole analogue, known as triazatetrabenzcorrole (TBC). Fujiki et al. were the first to report the confirmed synthesis of a TBC ring in 1986, prepared via the ring-contraction of the germanium phthalocyanine ($PcGeCl_2$) by reaction with $NaBH_4$, resulting in the corresponding metalloid TBC (TBCGeOH).[16] Later, Liu et al.[17] and Hanack et al.[18] showed that ring contraction of certain phthalocyanine precursors could be affected by reaction with PBr_3 and Si_2Cl_6.[18,19] Interestingly, Gouterman reported the synthesis of phosphorus(III) and phosphorus(V) phthalocyanines by a similar reaction pathway as early as 1981, with the observation that the PcP^V species exhibited an unexpectedly red-shifted Soret band at 422 nm.[20] It has since been shown that this product was in fact a phosphorus(V) TBC compound.[18] Other than these few earlier studies, the synthesis and properties of TBCs have remained largely unexplored, which is surprising given the importance of phthalocyanines and their analogues in the electronics, environmental and healthcare fields.[21−26]

Herein we report the synthesis of a new series of phosphorus(V) TBC compounds prepared via the ring-contraction of octabutoxy-phthalocyanine $(BuO)_8PcH_2$ and octachloro-octabutoxy-phthalocyanine $(BuO)_8Cl_8PcH_2$ precursors. In the earlier work on TBCs, the Pc precursors that were employed had certain drawbacks in regards to their solubility properties or their method of synthesis. The Pc starting materials utilized in this study are quite easy to synthesize, exhibit excellent solubility in common organic solvents, and, as expected, confer the same desirable solubility properties on the resultant TBC products. The new TBC compounds described here have been fully characterized by UV−vis, ^{1}H NMR, ^{31}P NMR, and MALDI-MS, and electrochemistry. We have shown that subtle modifications in the conditions of the synthesis and purification of the TBC-(P^V) compounds determines the phosphorus coordination number and identity of the axial ligands. The optical and electrochemical properties of the TBC compounds are assessed and compared with each other and with the relevant Pc precursors. In addition, a phosphorus(V) phthalocyanine, $[(BuO)_8PcP(OCH_3)_2]^+$, was synthesized in order to have a direct Pc analogue for comparison of spectroscopic features. Although other metalloid Pc compounds are known,[27] examples of bona fide phosphorus phthalocyanines are extremely rare.[18,28] Thus, the synthesis, characterization, and physical properties (e.g., UV−vis, electrochemistry) of $[(BuO)_8PcP(OCH_3)_2]^+$ are of interest in their own right as well as for comparative purposes with the TBCs. Of particular note, a remarkably red-shifted Q-band (λ_{max} 889 nm) has been found for this compound.

Experimental Section

Materials and General Methods. The synthesis of compounds **1** and **6** has been reported previously.[29] However, in this work these compounds were described as part of the synthesis of a large series of phthalocyanine derivatives, and detailed experimental procedures, including full spectroscopic characterization of **1** and **6**, were not given. Thus, we describe here a detailed synthesis and complete characterization of **1** and **6**. Solvent distillations and synthetic procedures were carried out under an argon atmosphere unless otherwise noted. Pyridine was purchased from Aldrich and distilled from calcium hydride. Phosphorus tribromide and phosphorus oxychloride were purchased from Acros Organics and stored under an argon atmosphere. Deuterated chloroform was purchased from Aldrich and stored over molecular sieves. Methanol was purchased from Aldrich and distilled from molecular sieves. Silica gel, 200−

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300 mesh, from Natland International, was used for column chromatography. All other chemicals and solvents were purchased from commercial sources and used without further purification.

1,4,8,11,15,18,22,25-Octabutoxyphthalocyanine, $(BuO)_8PcH_2$ (1). A 250 mL flask containing 3,6-dibutoxy-1,2-benzene dicarbonitrile (3.036 g, 11.15 mmol) and *n*-butanol (15 mL) was heated to 60 °C. Upon complete dissolution of the dinitrile, chopped lithium metal (2.25 g, 445 mmol) was slowly added to the vigorously stirred solution. Upon complete addition of the lithium, the mixture was heated to 118 °C and allowed to stir under argon for 1 h. After 1 h, the solution was cooled to room temperature, diluted with acetic acid (150 mL), and filtered. The filtrate was stirred for 0.5 h and the solvent subsequently removed under reduced pressure. The resulting solid was dissolved in CH_2Cl_2, placed in a separatory funnel, and washed with several portions of equal volume of a saturated aqueous $NaHCO_3$ solution. Washing with bicarbonate was stopped once gas bubbles were no longer observed after mixing. The organic layer was collected, dried with Na_2SO_4, and filtered. The filtrate was reduced to dryness and recrystallized from CH_2Cl_2/MeOH to give **1** as a dark green crystalline solid (1.88 g, 62%). ^{1}H NMR ($CDCl_3$): δ 7.59 (s, 8H), 4.85 (t, 16H, $J = 7.6$ Hz), 2.23 (sxt, 16H, $J = 7.2$ Hz), 1.64 (quin, 16H, $J = 7.2$ Hz), 1.08 (t, 24H, $J = 7.2$ Hz). UV−vis (toluene) λ nm ($\epsilon \times 10^{-3}$): 330 (54.9), 407 (24), 739 (113), 760(132). Anal. Calcd for $C_{64}H_{82}N_8O_8$: C, 70.42; H, 7.58; N, 10.27. Found: C, 70.46; H, 7.54; N, 10.22. MALDI (*m*/*z*) 1090.7 [$M^{+\bullet}$].

Dimethoxyphosphorus(V) 1,4,8,11,15,18,22,25-Octabutoxyphthalocyanine Hydroxide, $[(BuO)_8(Pc)P(OCH_3)_2]^+OH^-$ (2). $(BuO)_8PcH_2$ (0.4 g, 0.37 mmol) was placed in a 50 mL flask equipped with a condenser and gas inlet adapter. Amounts of pyridine (10 mL) and $POCl_3$ (4.0 g, 2.4 mL, 26.1 mmol) were added sequentially to the flask, and the solution stirred at 118 °C for 3 h. The volatiles were then removed by vacuum distillation, and the resulting solid was quenched with a solution of CH_2Cl_2/MeOH (50/50 v/v). This mixture was allowed to stir for 0.5 h, reduced to dryness, then redissolved in CH_2Cl_2, and washed twice with deionized water. The lower (organic) layer was collected and reduced to dryness to yield a purple/brown product. The resulting solid was taken up in a minimal amount of CH_2Cl_2 and then precipitated by the addition of *n*-hexane to yield **2** as a light purple solid (0.29 g, 67%). ^{1}H NMR ($CDCl_3$): δ 7.78 (s, 8H), 4.74 (t, 16H, $J = 7.6$ Hz), 2.19 (sxt, 16H, $J = 7.6$ Hz), 1.63 (quin, 16H, $J = 7.6$ Hz), 1.08 (t, 24H, $J = 7.6$ Hz), −0.38 (d, 6H, $^3J_{PH} = 26.4$ Hz). ^{31}P NMR (400 MHz, $CDCl_3$): δ −179.8. UV−vis (CH_3OH) λ nm ($\epsilon \times 10^{-3}$): 366 (31), 559 (14) 785 (25), 889 (91). MALDI (*m*/*z*) 1181.6 [M^+].

Dimethoxyphosphorus(V) 3,6,10,13,17,20,24,27-Octabutoxytriazatetrabenzcorrole, $(BuO)_8(TBC)P(OCH_3)_2$ (3). $(BuO)_8PcH_2$ (2.1 g, 1.92 mmol) was placed in a 100 mL flask equipped with a condenser and gas inlet adapter and dissolved in 7.5 mL of pyridine. An amount of PBr_3 (5.43 mL, 57.6 mmol) was added and the resulting solution heated to 118 °C and stirred for 1 h. After 1 h, the volume of the reaction mixture was reduced by vacuum distillation to 1−2 mL and then treated with a 50/50 solution of CH_2Cl_2/MeOH. The resulting solution was filtered and the solvent subsequently removed in vacuo. The green solid was dissolved in CH_2Cl_2 and filtered to remove excess pyridinium bromide as a white crystalline solid. The filtrate was reduced in volume under reduced pressure and loaded onto a silica gel column for purification with 95/5 CH_2Cl_2/MeOH as the eluent. The first dark purple band to elute was collected and dried under vacuum to give **3** as a shiny green solid (1.77 g, 79%). ^{1}H NMR ($CDCl_3$): δ 7.63−7.77 (m, 8H), 5.05 (m, 16H), 2.35 (m, 16H), 1.84 (m, 16H), 1.19 (m, 24H), −1.72 (d, 6H, $^3J_{PH} = 24.0$ Hz). ^{31}P NMR (400 MHz, $CDCl_3$): δ −186.1. Anal. Calcd for $C_{66}H_{86}N_7O_{10}P_1$: C, 67.84; H, 7.41; N, 8.39. Found: C, 67.89; H, 7.48; N, 8.45. UV−vis (CH_2Cl_2) λ nm ($\epsilon \times 10^{-3}$): 331 (29), 495 (52), 520 (64), 653 (23), 682 (37), 720 (73). MALDI *m*/*z* 1167.7 [$M^{+\bullet}$].

Hydroxyphosphorus(V) 3,6,10,13,17,20,24,27-Octabutoxytriazatetrabenzcorrole Hydroxide, $[(BuO)_8(TBC)P(OH)]^+OH^-$ (4). This compound was prepared as described for **3** except for the following modifications. After reaction with PBr_3, approximately $^3/_4$ of the solvent was removed under reduced pressure and the solid treated with a 50/50 solution of CH_2Cl_2/EtOH. The solution was filtered and reduced to dryness to give a dark green residue, which was dissolved in CH_2Cl_2 and purified on a silica gel column using 85/10/5 CH_2Cl_2/acetone/ethyl acetate as the eluent. A dark purple band was collected and concentrated to dryness to give **4** as a shiny, purple-green solid (1.74 g, 75%). ^{1}H NMR ($CDCl_3$): δ 7.64 (m, 8H), 4.89 (m, 16H), 2.34 (m, 16H), 1.76 (m, 16H), 1.18 (m, 24H). ^{31}P NMR (400 MHz, $CDCl_3$): δ −105.1. Anal. Calcd for $C_{64}H_{82}N_7O_{10}P_1$: C, 67.39; H, 7.25; N, 8.60. Found: C, 67.06; H, 7.43; N, 8.32. UV−vis (CH_2Cl_2) λ nm ($\epsilon \times 10^{-3}$): 334 (39), 365 (34), 490 (shoulder, 43), 526 (55), 656 (shoulder, 25), 690 (shoulder, 35), 726 (61). MALDI *m*/*z* 1139.7 $\{[(BuO)_8(TBC)P(OH)][OH]\}^+$.

4,5-Dichloro-3,6-dibutoxy-1,2-benzenedicarbonitrile (5). This procedure is modified from one previously reported.[30] Over the course of 10 min, 12.5 mL of H_2O was added dropwise to a vigorously stirring slurry of diethyl ether (100 mL), $Na_2S_2O_5$ (20.95 g, 110 mmol), and 2,3-dichloro-5,6-dicyano-1,4 benzoquinone (25.0 g, 110 mmol). After the addition of water, the reaction was stirred for an additional 0.5 h and the solvent subsequently removed under reduced pressure. A solution of KOH(aq) (150 mL of a 1.9 M solution) was then added to the dried product and stirred for 10 min after which tetrabutylammonium bromide (7.1 g, 22 mmol) and 1-iodobutane (50 g, 271 mmol) were added. The reaction mixture was allowed to reflux under argon for 6 h. The organic layer was collected and reduced to dryness, and the resulting solid was purified by crystallization from acetone to give **5** as a white crystalline solid. (33.41 g, 89%). ^{1}H NMR ($CDCl_3$): δ 4.23 (t, 4H), 1.87 (sxt, 4H), 1.58 (quin, 4H), 1.01 (t, 6H). FAB-MS *m*/*z* 341.1 [$M + H^+$].

1,4,8,11,15,18,22,25-Octabutoxy-2,3,9,10,16,17,23,24-octachlorophthalocyanine, $(BuO)_8Cl_8PcH_2$ (6). A 250 mL flask containing 4,5-dichloro-3,6-dibutoxy-1,2-benzene-dicarbonitrile (5.2 g, 15.3 mmol) and *n*-butanol (15 mL) was heated to 75 °C. Upon complete dissolution of the dinitrile, chopped lithium metal (4.0 g, 570 mmol) was slowly added to the vigorously stirred solution. Upon complete addition of the lithium, the mixture was heated to reflux and allowed to stir under argon for 1 h. The reaction mixture was then cooled to room temperature and the solvent removed under reduced pressure. The resulting solid was dissolved in acetic acid, allowed to stir for 15 min and filtered, and the filtrate was subsequently collected and dried under reduced pressure. The resulting solid was then redissolved in CH_2Cl_2 and filtered to remove excess lithium acetate. The filtrate was collected, placed in a separatory funnel, and washed with several portions of equal volume of aqueous $NaHCO_3$ until no more gas was evolved upon addition of the bicarbonate solution. The organic layer was collected, dried with Na_2SO_4, and filtered. The filtrate was reduced to dryness and recrystallized from CH_2Cl_2/MeOH to give **6** as a light green crystalline solid (2.19 g, 42%). ^{1}H NMR ($CDCl_3$): δ 5.05 (t, 16H, $J = 7.0$ Hz), 2.29 (sxt, 16H, $J = 7.2$ Hz), 1.75 (quin, 16H, $J = 7.6$

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Hz), 1.14 (t, 24H, $J = 7.2$ Hz). Anal. Calcd for $C_{64}H_{74}N_8O_8Cl_8$: C, 56.23; H, 5.47; N, 8.22. Found: C, 57.17; H, 5.69; N, 8.11. UV−vis (CH_2Cl_2) λ nm ($\epsilon \times 10^{-3}$): 331 (61), 680 (52), 769 (128). MALDI *m*/*z* 1367.4 [$M^{+\bullet}$].

Hydroxyphosphorus(V) 3,6,10,13,17,20,24,27-Octabutoxy-4,5,11,12,18,19,25,26-octachlorotriazatetrabenzcorrole Hydroxide, $[(BuO)_8Cl_8(TBC)P(OH)]^+OH^-$ (7). To a 100 mL flask was added $BuO_8Cl_8PcH_2$ (1.3 g, 0.95 mmol). The flask was purged several times with argon, and pyridine (5 mL) was transferred into the reaction vessel. An amount of PBr_3 (2.7 mL, 7.78 g, 28.6 mmol) was then added and the resulting solution heated to 118 °C and stirred for 0.75 h. After 0.75 h, approximately $^1/_2$ of the solvent was allowed to evaporate under a flow of argon. The mixture was then poured into a water/ice bath and the resulting suspension filtered to give a dark green solid. The solid was purified on a silica gel column using 90/10 CH_2Cl_2/acetone as the eluent. The purple/green band was collected and concentrated producing **7** as a dark purple solid (0.52 g, 39%). ^{1}H NMR ($CDCl_3$): δ 5.04 (br m, 16H), 2.26 (m, 16H), 1.72 (m, 16H), 1.09 (m, 24H). ^{31}P NMR (400 MHz, $CDCl_3$): δ −105.13. UV−vis (CH_2Cl_2) λ nm ($\epsilon \times 10^{-3}$): 349 (28.9), 500 (61), 652 (16.7), 685 (25.7), 722 (57.8). MALDI *m*/*z* 1415.4 $\{[(BuO)_8Cl_8(TBC)P(OH)][OH]\}^+$.

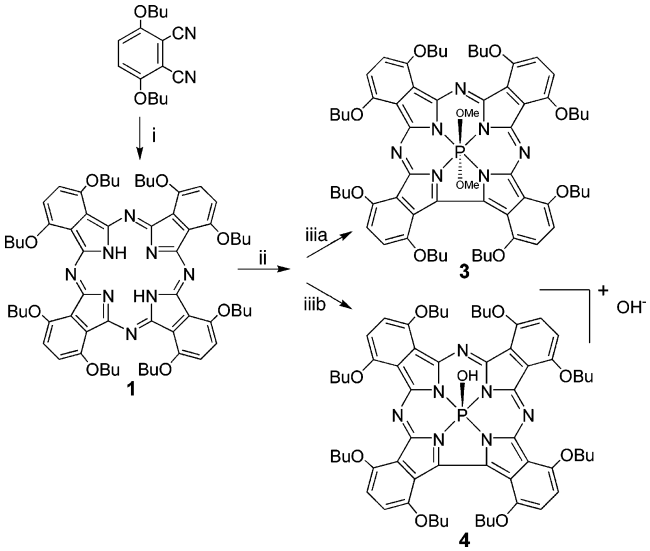
Electrochemistry. Cyclic voltammograms were measured with an EG&G Princeton Applied Research potentiostat/galvanostat model 263A at scan rates 0.5−0.025 V s^{-1}. A three-electrode configuration made up of a platinum working electrode, a Ag/AgCl reference electrode (3.5 M KCl), and a platinum wire auxiliary electrode was employed. Measurements were performed at ambient temperatures under nitrogen with 0.10 M tetra-*n*-butylammonium hexafluorophosphate (recrystallized 3 times from ethanol and stored in a vacuum oven at 50 °C for 5 days prior to use) in CH_2Cl_2 as the supporting electrolyte. The ferrocenium/ferrocene couple ($FeCp_2^{+/0}$) was used as an external reference.

Physical Measurements. ^{1}H NMR spectra were recorded on a Varian Unity plus 400 spectrometer (400 MHz) at ambient probe temperature with either 0.1% tetramethylsilane or residual proteochloroform used as the internal reference. ^{31}P NMR spectra were recorded on the same spectrometer with H_3PO_4 as the external reference. Electronic absorption spectra were taken on an Agilent 8453 UV−vis spectrometer. Electron paramagnetic resonance (EPR) spectra were obtained on a Bruker EMX EPR spectrometer controlled with a Bruker ER 041 X G microwave bridge. The field/frequency was calibrated by measuring the *g* value of DPPH. FAB mass spectra were recorded at the Mass Spectrometry Laboratory, Department of Chemistry, Johns Hopkins University, using a VG analytical 70-S mass spectrometer. The MALDI data were collected on a Voyager DE-STR (Applied Biosystems) at the AB Mass Spectrometry/Proteomics facility at the Johns Hopkins School of Medicine.

Results and Discussion

Synthesis. (a) Design and Preparation of the Phthalocyanine Precursor $(BuO_8)PcH_2$ (1). The octabutoxy-substituted phthalocyanine precursor **1** was prepared as shown in Scheme 1, following a modified method of Cook.[29] The 3,6-dibutoxy-phthalonitrile was converted to **1** by a Li-templated macrocyclization reaction in refluxing butanol. The initial product of the cyclization is most likely $Li_2[(BuO)_8Pc]$, which is then rapidly protonated upon addition of acetic acid to give $(BuO)_8PcH_2$. The cyclization reaction was carried out on a larger scale than that described previously (11.5 mM vs 3.8 mM of phthalonitrile starting material), and an important modification in the workup of the reaction was introduced. We found that washing the crude product with a saturated sodium bicarbonate solution, instead of 10% HCl as described by Cook, resulted in significantly higher yields (62% versus 21%). Purification of $(BuO)_8PcH_2$ was accomplished by recrystallization from CH_2Cl_2/MeOH.

Scheme 1 [a]

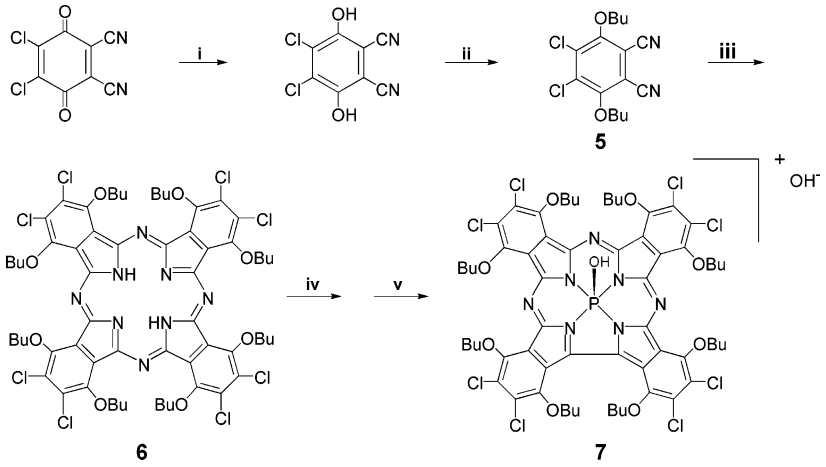


[a] (i) Li(s), *n*-butanol, 118 °C, 1 h (62%); (ii) PBr_3, pyridine, 118 °C, 1 h; (iiia) MeOH, CH_2Cl_2, rt (79%); (iiib) EtOH, CH_2Cl_2, rt (75%).

The octabutoxy-substituted Pc **1** was selected as the best phthalocyanine candidate for ring-contraction studies because of its excellent solubility in common organic solvents, and because it is quite easy to synthesize. Previously, Fujiki,[16] Yao,[17] and Hanack[18] had described the synthesis of different metalated (e.g., P, Ge, Si) TBCs from the ring-contraction of the parent, unsubstituted phthalocyanine (PcH_2). The parent PcH_2 is notoriously insoluble in all common organic solvents, making it very difficult to purify and characterize, and we suspected that the TBC product would show similar solubility problems. Thus, we sought substituted Pc precursors that would be freely soluble in organic solvents. The latter study by Hanack showed that in addition to PcH_2, the substituted Pc's, $(t\text{-Bu})_4PcH_2$, $(C_3H_7)_8PcH_2$, and $(C_5H_{11})_8PcH_2$, could be converted to ring-contracted TBC products upon treatment with PBr_3. Although the ring-contractions proceeded smoothly and the alkyl-substituted phthalocyanines had better solubility properties than the parent PcH_2, these precursors still had certain drawbacks. For the tetra-*tert*-butyl precursor $(t\text{Bu})_4PcH_2$, ring-contraction led to a mixture of regioisomers, and in the case of the octaalkyl-substituted Pc's $(C_3H_7)_8PcH_2$ and $(C_5H_{11})_8PcH_2$, a lengthy synthesis is required for their preparation.[31] We were thus motivated to find a phthalocyanine starting material that is easy to synthesize and could be expected to result in a triazatetrabenzcorrole as a single regioisomer with excellent solubility in common organic solvents. The octabutoxy-substituted phthalocyanine **1** was selected as a potentially ideal TBC starting material. The phthalonitrile precursor needed to prepare **1** is commercially available, and the

(31) Pawlowski, G.; Hanack, M. *Synthesis* **1980**, 287−289.

Scheme 2 [a]



[a] (i) H_2O, $Na_2S_2O_5$, diethyl ether, 0.5 h (99%); (ii) KOH(aq), TBAB, 1-iodobutane, 100 °C, 6 h (90%); (iii) Li(s), *n*-butanol, 118 °C, 1 h (42%); (iv) PBr_3, pyridine, 118 °C, 1 h; (v) H_2O/ice (39%).

symmetrical substitution pattern of the butoxy substituents ensures a single regioisomer for both Pc and TBC products. In addition, Pc **1** is freely soluble in many common organic solvents (e.g., hexane, CH_2Cl_2, ethyl acetate).

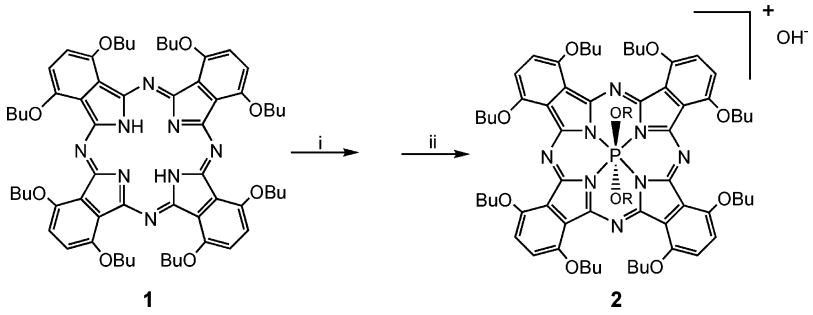
(b) Synthesis of Triazatetrabenzcorroles $(BuO)_8(TBC)P(OCH_3)_2$ (3) and $[(BuO)_8(TBC)P(OH)]^+OH^-$ (4). Ring-Contraction of $(BuO)_8PcH_2$ (1). An obvious problem with using **1** as a TBC precursor is the possible steric repulsion between butoxy substituents that might be expected to interfere with ring-contraction to give the triazatetrabenzcorrole nucleus. We were pleased to find that Pc **1** undergoes facile ring-contraction to give the triazatetrabenzcorroles **3** and **4**. The synthesis of TBCs **3** and **4** is shown in Scheme 1. The ring contraction of **1** was induced by refluxing with excess PBr_3 in pyridine for 1 h under the strict exclusion of air and water. In order to ensure a good yield of TBC, the pyridine must be carefully distilled over CaH_2, and the phthalocyanine starting material must be dried in a heated (50 °C) vacuum oven for several hours immediately prior to use. It is likely that any trace water in the reaction mixture rapidly reacts with the PBr_3 reagent to give $POBr_3$, which then reacts with **1** via phosphorus insertion to give phosphorus phthalocyanine instead of the ring-contracted product, resulting in a lower yield of TBC. At the end of the reaction, the excess PBr_3 must be neutralized. If the reaction mixture is quenched with CH_2Cl_2/MeOH (50/50 v/v), the dimethoxy compound $(BuO)_8(TBC)P(OMe)_2$ (**3**) is obtained after purification by silica gel chromatography (95/5 CH_2Cl_2/MeOH as the eluent) in good yield (79%). In contrast, if EtOH is used in place of MeOH as the quenching agent (CH_2Cl_2/EtOH (50/50 v/v), the dihydroxy compound $[(BuO)_8(TBC)P(OH)]^+OH^-$ (**4**) is isolated instead of the expected diethoxy product $(BuO)_8(TBC)P(OEt)_2$. Purification of **4** was accomplished by chromatography (SiO_2, CH_2Cl_2/acetone/ethyl acetate 85/10/5) to give **4** in good yield (75%).

(c) Axial Ligation at the Phosphorus Center. The earlier work on PBr_3-induced ring-contraction describes the formation of P(V)═O products,[18] as opposed to P−OH or P−OR products. The terminal oxo ligand was presumably derived from quenching the reaction mixture with water after refluxing in pyridine. Initially, we followed this procedure and attempted to quench the ring-contraction reaction of **1** with water but found that this method gave a large amount of insoluble solid byproducts, making it difficult to extract and isolate the desired TBC product and invariably resulted in low yields. However, formation of the insoluble byproducts was avoided by quenching the reaction with a mixture of alcohol (MeOH or EtOH) and methylene chloride, affording the TBC compounds **3** and **4** in good yields. Although the use of MeOH leads to axial methoxide ligands attached to the phosphorus atom, addition of wet EtOH at the end of the reaction resulted in the formation of the dihydroxy compound **4**, and not the expected bis(ethoxide) product. However, if water is excluded from the quenching step by using dry EtOH that has been freshly distilled over CaH_2 and kept under argon, evidence for the presence of axial ethoxy substituents is obtained by ^{1}H NMR spectroscopy. Peaks at δ −1.93 and −2.15 ppm are observed, corresponding to axial $-OCH_2CH_3$ resonances that are clearly upfield-shifted by ring current effects. Also, purification of the initial dihydroxy product using ethanol/CH_2Cl_2 mixtures as eluent on silica gel leads to evidence for $-OCH_2-CH_3$ axial ligands by ^{1}H NMR spectroscopy. These data show that EtOH will eventually exchange with the axial OH group to give a P−OEt ligated center. Interestingly, we have not seen any evidence for the P═O ligation for any of our TBC derivatives (vide infra).

(d) Synthesis of $(BuO)_8Cl_8PcH_2$ (6). There has been a great deal of interest in electron-poor porphyrinoid species, and in particular, much effort has gone into the synthesis of polyhalogenated systems.[32−36] We thought it of interest to determine the effects of halogenation on the physical

(32) Birnbaum, E. R.; Hedge, J. A.; Grinstaff, M. W.; Schaefer, W. P.; Henling, L.; Labinger, J. A.; Bercaw, J. E.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 3625−3632.
(33) Takeuchi, T.; Gray, H. B.; Goddard, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 9730−9732.
(34) Biffinger, J. C.; Sun, H.; Nelson, A. P.; DiMagno, S. G. *Org. Biomol. Chem.* **2003**, *1*, 733−736.
(35) Dolphin, D.; Traylor, T. G.; Xie, L. Y. *Acc. Chem. Res.* **1997**, *30*, 251−259 and references therein.
(36) Terazono, Y.; Dolphin, D. *J. Org. Chem.* **2003**, *68*, 1892−1900.

Scheme 3 [a]



1 2

[a] (i) $POCl_3$, pyridine, 118 °C, 3 h; (ii) 50/50 CH_2Cl_2/MeOH, 0.5 h (67%).

properties and reactivity of the Pc and TBC compounds described in this work. We realized it would also be of interest to show that the scope of the ring-contraction reaction could be expanded to include phthalocyanine substituted at all 16 peripheral positions, which has not been demonstrated thus far. The synthesis of the phthalocyanine precursor **5** was accomplished in 2 steps as shown in Scheme 2 via a modified literature procedure.[30] Reduction of dicyanodichlorobenzoquinone (DDQ) to the dihydroquinone and subsequent alkylation of the dihydroquinone with 1-iodobutane affords **5** in good yield. We note that it is important to maintain efficient stirring of the reaction mixture at all times in order to keep the dihydroquinone suspended as a fine powder and prevent it from aggregating during the alkylation step. The alkylated product is then purified via recrystallization from acetone and used in the next step. Formation of **6** is carried out in refluxing *n*-butanol in the presence of Li^+. After workup, the Pc product **6** is purified by recrystallization from CH_2Cl_2/MeOH to yield a light green powder.

(e) Synthesis of $[(BuO)_8Cl_8(TBC)P(OH)]^+OH^-$ (7). The ring-contraction of **6** was induced by the addition of PBr_3, just as in the case of **1**, as shown in Scheme 2. The reaction was quenched with an ice/water mixture resulting in the precipitation of TBC **7**, which after purification was recovered in reasonable yield (39%). The successful use of an aqueous workup for **7** contrasts the results obtained during the synthesis of **3**, for which an aqueous workup resulted in insoluble byproducts and very poor yield. For the case of **7**, only a small amount of insoluble material was formed which did not interfere with the isolation of the product. The workup of the ring-contraction of **6** with alcohol (CH_2Cl_2/MeOH) did not result in an improvement in the yield. Purification by silica gel chromatography was carried out by using an acetone/CH_2Cl_2 solution as the eluent, rather than an ROH/CH_2Cl_2 solution, to avoid any axial ligand exchange with alcohols.

(f) Synthesis of $[(BuO)_8(Pc)P(OCH_3)_2]^+OH^-$ (2). The phosphorus phthalocyanine **2** was prepared in order to obtain a Pc analogue of the $(BuO)_8(TBC)(P^V)$ complexes for comparison of spectroscopic properties (NMR, UV−vis, electrochemistry). Insertion of phosphorus into the central cavity of **1** was accomplished by reacting the metal-free Pc with $POCl_3$ in pyridine under reflux for 3 h, as shown in Scheme 3. It was found that longer reaction times (>4 h) did not increase yields, and only resulted in partial degradation of the product. The use of $POCl_3$ in place of PBr_3 gives only the phosphorus phthalocyanine, and none of the ring-contracted product. A similar method of phosphorus insertion was used previously to prepare a phosphorus-containing alkyl-substituted phthalocyanine.[18] The reaction mixture was quenched with MeOH, which provided the axial methoxide ligands to the central phosphorus atom. The product was purified by via silica gel chromatography using 95/5 CH_2Cl_2/MeOH as the eluent. The purple band was collected and recrystallized from CH_2Cl_2/*n*-hexane to give **2** as a purple crystalline solid (67%).

Interestingly, although phosphorus porphyrins have been known for quite some time and there are many examples of such compounds, the first phosphorus phthalocyanines were not prepared until quite recently. To our knowledge, there are only three authentic Pc(P) compounds that have been reported to date outside of the patent literature, the tetra-^{t}Bu$_4$PcP^V(O)(OH),[28] dihydroxyphosphorus(V) phthalocyanine hydroxide, and dihydroxyphosphorus(V) 2,9,16,23-tetra-*tert*-butylphthalocyanine hydroxide.[18,28] An early report of the reaction of PBr_3 with PcH_2 claimed that Pc-P^{III} and Pc-P^V compounds had been synthesized,[20] but these compounds were later correctly identified as the ring-contracted TBC products.[18]

NMR Spectroscopy. (a) ^{1}H NMR Spectroscopy of $(BuO)_8(Pc)H_2$ (1), $[(BuO)_8(Pc)P(OCH_3)_2]^+OH^-$ (2), $(BuO)_8$-$(TBC)P(OCH_3)_2$ (3), and $[(BuO)_8(TBC)P(OH)]^+OH^-$ (4). The ^{1}H NMR spectra of **3** and **4** in $CDCl_3$ can be assigned on the basis of the spectra for **1** and **2**. For the symmetric Pc's **1** and **2**, the tautomerization rate of the internal N−H protons is likely to be fast, providing pseudo-4-fold symmetry (D_{4h}-symmetry)[37] and resulting in all aromatic protons appearing as two sharp singlets at δ 7.62 and 7.78 ppm, respectively. The symmetry is reduced for the ring contracted TBCs **3** and **4**, causing the resonances for the aromatic protons to appear as a multiplet at δ 7.63−7.77 ppm for both compounds. A second multiplet for **3** and **4** is centered at δ 5.05 and 4.89 ppm, respectively, and these peaks are assigned to the overlapping triplets from the four OCH_2− groups, which are expected to be inequivalent due to the C_{2v} symmetry of the TBC ring. The analogous protons in the symmetric Pc's **1** and **2** appear in the same region as well resolved triplets: δ 4.85 ppm, J = 7.6 Hz for **1** and δ 4.74 ppm, J = 7.6 Hz for **2**. The peaks for the remaining alkyl

(37) Cook, M. J.; Cracknell, S. J.; Moore, G. R.; Osborne, M. J.; Williamson, D. J. *Magn. Reson. Chem.* **1991**, *29*, 1053−1060.

Table 1. ^{31}P NMR Data and Structural Information for Selected P^V Phthalocyanines, Porphyrins, Corroles, and Triazatetrabenzcorroles[a]

compound	coordination no.	^{31}P NMR	X-ray	ref
$[(BuO)_8(Pc)P(OCH_3)_2]^+OH$ (**2**)	6	−179.8	no	this work
$(BuO)_8(TBC)P(OCH_3)_2$ (**3**)	6	−186.1	no	this work
$[(BuO)_8(TBC)P(OH)]^+OH^-$ (**4**)	5	−105.1	no	this work
$[(BuO)_8Cl_8(TBC)P(OH)]^+OH^-$ (**7**)	5	−105.1	no	this work
$[P(OH)_2(tBu_4Pc)](OH)$	6	−166.07	no	18
$PO(tBu_4TBC)$	6	−186.7	no	18
$[(TBP)_8CzP(OH)]OH$	5	−111.2	no	14
$(TBP)_8CzP(OCH_3)_2$	6	−192.1	yes	14
(OEC)P═O	6	−99.40	no	42
$[(EMC)P(OH)]^+Cl^-$	5	−102.5	yes	41
$[P(OEP)(CH_2CH_3)(OH)]^+ClO_4^-$	6	−179.8	yes	39
$[P(OEP)(C_6H_5)(OCH_2CH_2CH_3)]^+ClO_4^-$	6	−186.7	yes	39

[a] Abbreviations: tBu_4Pc = 2,9,16,23-tetra-*tert*-butylphthalocyanine, tBu_4TBC = 4,11,18,25-tetra-*tert*-butyltriazatetrabenzcorrole, $(TBP)_8Cz$ = octa-4-*tert*-butylphenylcorrolazine, OEC = octaethylcorrole, EMC = 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole, OEP = octaethylporphyrin.

protons of **3** and **4** appear as multiplets in the expected region δ 1.19−2.35 ppm. The resonances for the axial $-OCH_3$ ligands of **3** are shifted significantly upfield by the aromatic ring-current effect from the macrocycle, appearing as a doublet centered at −1.72 (d, J = 24 Hz), while the proton for the OH bound to the central phosphorus atom in **4** is not observed. Interestingly, the ring-current effect induced by the Pc macrocycle in $[(BuO)_8(Pc)P(OCH_3)_2]^+$ is considerably smaller; the methoxide resonance in **2** appears at δ −0.38 ppm (d, $^3J_{PH}$ = 26 Hz).

(b) ^{31}P NMR Spectroscopy of $[(BuO)_8(Pc)P(OCH_3)_2]^+OH^-$ (2), $(BuO)_8(TBC)P(OCH_3)_2$ (3), and $[(BuO)_8(TBC)P(OH)]^+OH^-$ (4). It is well established that the chemical shifts of phosphorus nuclei in ^{31}P NMR spectroscopy are sensitive to the coordination number of the phosphorus center.[38] In particular, for P^V porphyrins there is a clear trend for 6-coordinate phosphorus compounds $[(porph)P^V(L)_2]$ which predominantly appear at −180 to −200 ppm, whereas 5-coordinate compounds $[(porph)P^VL]$ are mostly found at −90 to −110 ppm.[38−40] In contrast to porphyrins, there are only a few examples of phosphorus(V) phthalocyanines and corroles for comparison, but these few examples appear to follow the same trends. Relevant literature values for Pcs, TBCs, corroles, and some representative porphyrins are given in Table 1 together with the experimental data for the phosphorus compounds examined in this study. It is also noted in Table 1 whether a particular entry has been characterized by X-ray crystallography. It is clear from the table that, in general, a 5-coordinate P^V TBC appears close to −100 to −111 ppm, and a 6-coordinate P^V TBC appears close to −185 to −190 ppm. We have previously used ^{31}P chemical shifts to determine the coordination number of the phosphorus triazacorroles $[(TBP)_8CzP(OH)]^+OH^-$, and $(TBP)_8CzP(OCH_3)_2$, which are also listed in Table 1 for comparison. This latter complex is one of only two corrole-type compounds for which the phosphorus coordination number has been determined by X-ray crystallography, the other of which is $[(EMC)P(OH)]^+$, and in both cases the solid state structures confirm the coordination number predicted by the ^{31}P chemical shifts. The TBC **3** exhibits an intense peak at −186 ppm confirming the assignment of a 6-coordinate structure, although a small minor peak at −105 ppm was also observed. The latter peak falls within the 5-coordinate range, being very close to the 5-coordinate corrole $[(EMC)P(OH)]Cl$ (δ −102.5 ppm)[41] as well as the 5-coordinate corrolazine $(TBP)_8(Cz)P(OH)^+$ (δ −111.2 ppm).[14] We interpret this peak as arising from a small amount of axial ligand dissociation, giving $[(BuO)_8(TBC)P(OCH_3)]^+$. The analogous Pc compound **2** exhibits only one peak at −179.8 ppm, indicating that Pc **2** is less prone to axial ligand dissociation. This observation can be rationalized by the fact that the overall cationic charge of **2**, which results from the Pc ring having one less negative charge than the TBC ring, produces an increased affinity for the negatively charged RO^- donors. For compound **4**, only one peak is observed at −105.1 ppm which is most similar to $[(EMC)P(OH)]^+$ and $[(TBP)_8CzP(OH)]^+$, and therefore it is safe to conclude that **4** also has a 5-coordinate, $[P^V-OH]^+$ structure. It must be noted that the $(tBu_4)(TBC)(P═O)$ compound prepared by Hanack and co-workers exhibits a 6-coordinate signal at −186 ppm, whereas the ^{31}P shift reported by Vogel and Kadish for the similar corrole complex (OEC)P═O is −99.4 ppm.[42] At this time, we cannot reconcile the upfield chemical shift observed for the latter complex.

(c) ^{1}H and ^{31}P NMR Spectroscopy of $(BuO)_8Cl_8(Pc)H_2$ (6) and $[(BuO)_8Cl_8(TBC)P(OH)]^+OH^-$ (7). Compound **6** displays a sharp triplet at δ 5.05 ppm assigned to the OCH_2 protons whereas in TBC **7** this resonance is split into several peaks between 4.8 and 5.6 ppm. These peaks are spread over a much wider range than the corresponding multiplet observed for TBCs **3** and **4**, indicating that, for **7**, the reduced symmetry of the macrocycle influences the OCH_2 resonances to a greater extent than found for **3** and **4**. The other alkyl resonances for **6** and **7** are found in the expected range. The ^{31}P NMR spectrum for **7** reveals a single peak at δ −105.1 ppm, which can be assigned to the 5-coordinate compound

(38) Mason, J. *Multinuclear NMR*; Plenum Press: New York, 1987.
(39) Akiba, K.; Nadano, R.; Satoh, W.; Yamamoto, Y.; Nagase, S.; Ou, Z.; Tan, X.; Kadish, K. M. *Inorg. Chem.* **2001**, *40*, 5553−5567.
(40) Rao, T. A.; Maiya, B. G. *Inorg. Chem.* **1996**, *35*, 4829−4836 and references therein.
(41) Paolesse, R.; Boschi, T.; Licoccia, S.; Khoury, R. G.; Smith, K. M. *Chem. Commun.* **1998**, 1119−1120.
(42) Kadish, K. M.; Ou, Z. P.; Adamian, V. A.; Guilard, R.; Gros, C. P.; Erben, C.; Will, S.; Vogel, E. *Inorg. Chem.* **2000**, *39*, 5675−5682.

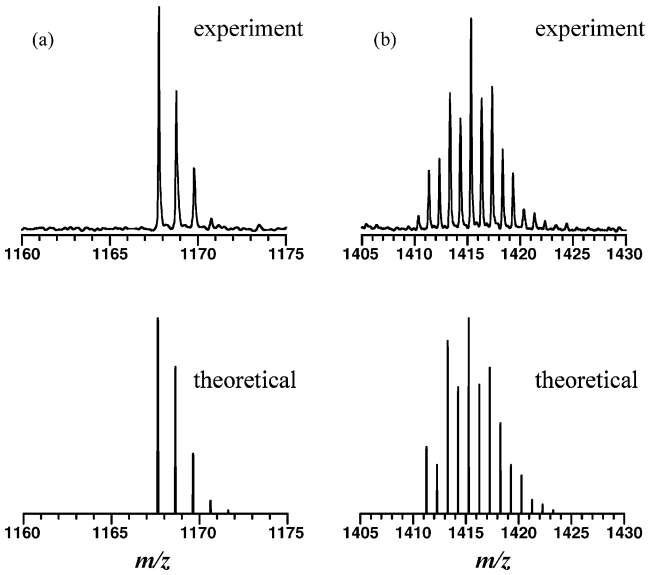


Figure 1. MALDI mass spectra (norharman matrix, positive ion mode) of the molecular ion regions and theoretical isotopic distributions for (a) **3**, $(BuO)_8(TBC)P(OCH_3)_2$, and (b) **7**, $[(BuO)_8Cl_8(TBC)P(OH)]^+OH^-$.

$(BuO)_8Cl_8(TBC)P(OH)^+$ on the basis of the ^{31}P NMR assignments discussed in the previous section.

MALDI Mass Spectroscopy of Phthalocyanines and Triazatetrabenzcorroles. We have found MALDI mass spectroscopy to be very useful for characterizing the structures of the new compounds synthesized in this study, and in particular, for identifying the axial ligands attached to the central phosphorus ion in the TBC(P^V) and Pc(P^V) compounds. The characterization of phthalocyanines **1**, **2**, and **6** by MALDI-MS (positive ion mode) resulted in well-resolved isotopic envelopes centered at 1090.7, 1181.6, and 1367.4 *m*/*z*, respectively. These peaks correspond to the molecular ions $M^{+\bullet}$ ($M = (BuO)_8PcH_2$ or $(BuO)_8Cl_8PcH_2$) and M^+ ($M = (BuO)_8(Pc)P(OCH_3)_2$). The assignment of $M^{+\bullet}$ for **1** and **6** corresponds to the phthalocyanine radical cation, which is the dominant intact molecule ion species observed in the mass spectrum. Detailed MALDI studies on porphyrins, phthalocyanines, and multiporphyrin arrays have shown that the radical cation $M^{+\bullet}$, as opposed to protonated $[M + H]^+$, is often the dominant ionized species observed for these types of compounds.[43,44] A cluster centered around the radical cation for TBC **3** at 1167.7 *m*/*z* is also observed in the MALDI-MS, and this spectrum is shown in Figure 1a together with the corresponding simulation. Interestingly, for TBCs **4** and **7**, the major species observed in the MALDI corresponds to the intact ion pair $([(TBC)P(OH)](OH))^+$, and the spectrum for the octachloro-substituted TBC **7** is shown in Figure 1b together with its simulation. As can be seen in the figure, the complex isotopic envelope for **7** due to the eight Cl substituents matches nicely with the theoretical simulation. Observance of intact ion pairs in MALDI-MS is not uncommon,[45] and we suggest that the facile ionization of the TBC as already noted results in the formally dicationic species $[(BuO)_8Cl_8(TBC)P(OH)]^{2+}$, which then has a greater attraction for the OH^- counterion leading to the observance of the intact ion pair.

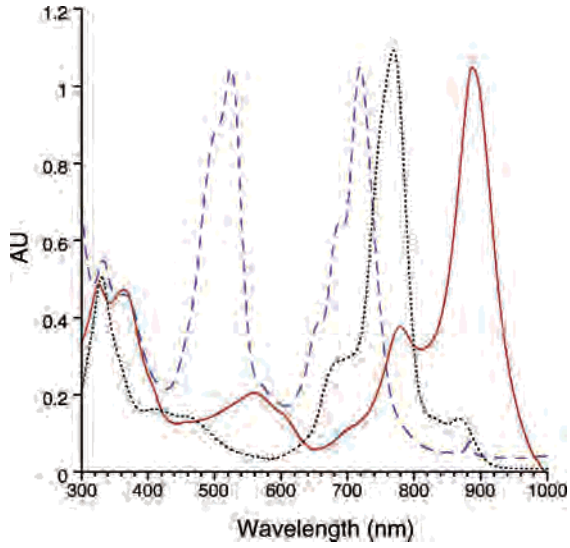


Figure 2. UV−vis spectra of **1**, $(BuO)_8PcH_2$, (5.3×10^{-6} M) in CH_2Cl_2 (black, ···), **2**, $[(BuO)_8(Pc)P(OCH_3)_2]^+OH^-$, ($3.3 \times 10^{-5}$ M) in CH_3OH (red, —), and **3**, $(BuO)_8(TBC)P(OCH_3)_2$, (1.44×10^{-5} M) in CH_2Cl_2 (blue, - - -).

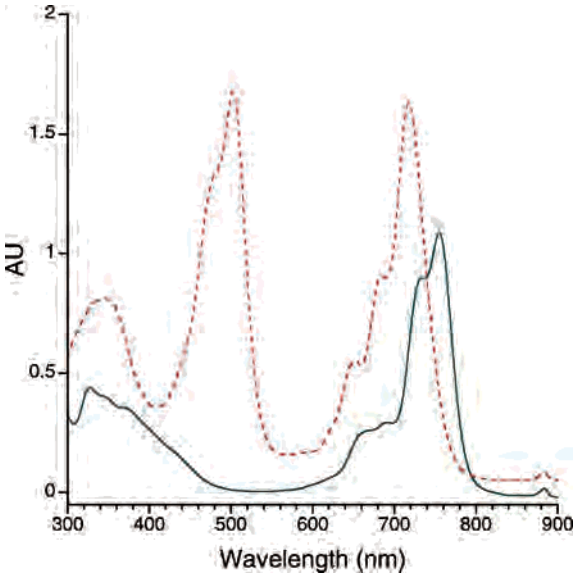


Figure 3. UV−vis spectra of **6**, $(BuO)_8Cl_8PcH_2$, (6.7×10^{-6} M) in CH_2Cl_2 (green, —) and **7**, $[(BuO)_8Cl_8(TBC)P(OH)]^+OH^-$, ($1.47 \times 10^{-6}$ M) in CH_2Cl_2 (red, - - -).

UV−Vis Spectroscopy of Phthalocyanines. $(BuO)_8PcH_2$ (1), $[(BuO)_8(Pc)P(OCH_3)_2]^+OH^-$ (2), and $(BuO)_8Cl_8PcH_2$ (6). The UV−vis spectra of phthalocyanines **1** and **2** are shown in Figure 2, and the spectrum for **6** is shown in Figure 3. All three compounds exhibit Soret (near-UV) and Q-type (visible) bands that are typical of $18\pi e^-$ aromatic Pc systems. These bands can be assigned by using the simple four-orbital model put forth by Gouterman, in which the Soret arises from an $e_g(LUMO) \leftarrow a_{2u}(HOMO - 1)$ transition and the Q-band stems from an $e_g(LUMO) \leftarrow a_{1u}(HOMO)$ transition

(43) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W. Z.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 283−291.
(44) Stulz, E.; Mak, C. C.; Sanders, J. K. M. *J. Chem. Soc., Dalton Trans.* **2001**, 604−613.
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(in D_{4h} symmetry).[46] A previous study on various 3′,6′-alkoxy-substituted Pc's showed that the alkoxy substituents in these positions caused a marked red-shift in the Q-band as compared to that of unsubstituted Pc.[29,47] Indeed, the Q-band of **1** in CH_2Cl_2 is found at 760 nm, compared to 698 and 663 nm (split Q-band in chloronaphthalene) for unsubstituted PcH_2.[25,48] Curiously, the positions of the Soret and Q-bands for octachloro-substituted **6** in Figure 3 are nearly the same as those of **1**. This finding contrasts the fact that the Cl substituents have a significant effect on the redox couples as shown in the electrochemical section (vide infra) and, thus, would be expected to have an effect on the electronic transitions as well.

As seen in Figure 2, upon insertion of a phosphorus(V) center into Pc **1**, the Q-band is further red-shifted dramatically by 129 nm, to give λ_{max} 889 nm for compound **2**. Such a large red-shift was quite unexpected, given that the few other known PcP^V compounds show only modest blue-shifts in the Q-band region compared to the corresponding metal-free phthalocyanine (e.g., for 2,9,16,23-tetra-*tert*-butyl-phthalocyanine, $\lambda_{max}(Q) = 695$ nm, and for oxophosphorus 2,9,16,23-tetra-*tert*-butyl-phthalocyanine hydroxide, $\lambda_{max}(Q) = 680$ nm).[28] The red-shift caused by the insertion of phosphorus into Pc **1** is even larger than that caused by increasing the size of the entire π-conjugation system, as seen by comparing the Q-band for (BuO_8)(naphthalocyanine)-H_2, at 867 nm,[48] which is shifted by 107 nm to longer wavelength compared to the Q-band seen for $(BuO)_8PcH_2$. To the best of our knowledge, the Q-band absorption of compound **2** represents the longest Q-band wavelength absorption in a phthalocyanine yet studied. Compounds with absorption into the near infrared are of particular interest regarding medical, electronic, and military applications.[49−51] For example, compounds with absorption in the range 600−850 nm are of potential use in photodynamic therapy (PDT) as these wavelengths most satisfactorily penetrate human tissue.[52,53] It is possible that compound **2** could have some utility in these regards.

UV−Vis Spectroscopy of Triazatetrabenzcorroles. $(BuO)_8(TBC)P(OCH_3)_2$ (3), $[(BuO)_8(TBC)P(OH)]^+OH^-$ (4), and $[(BuO)_8Cl_8(TBC)P(OH)]^+OH^-$ (7). The UV−vis spectra of compounds **3** and **4** are nearly identical, and thus, only the spectrum for **3** is shown in Figure 2. The spectrum for the chloro-substituted TBC **7**, which is also quite similar to **3** and **4**, is shown in Figure 3. These spectra have some similarities with the spectra previously reported for other TBC macrocycles, including a red-shift in the Soret band and a blue-shift in the Q-band compared to the Pc precursor.[16−18] For example, the Soret band reported for the phthalocyanine $(^iPrO)_4PcH_2$ is located at 338 nm, while the Soret band reported for the analogous TBC compound $(^iPrO)_4$(TBC)P(O) has λ_{max} 450 nm. The Q-band (658 nm) for this TBC compound displays a blue-shift compared to the Pc (708 nm).[17] Likewise, the germanium TBC compound TBCGeOH displays a 78 nm red-shift in the Soret band (444 nm) compared to PcH_2 (366 nm), and a 35 nm blue-shift in the Q-band (698 to 663 nm).[16] The former red-shift is likely a result of the destabilization of the HOMO − 1 (a_{2u}) orbital caused by the removal of a *meso*-nitrogen atom. In addition, we have shown that the related corrolazine $[(TBP)_8CzP(OH)]^+$ exhibits a 70 nm red-shift in the Soret-band and a 48 nm blue-shift in the Q-band compared to the tetraazaporphyrin precursor. Interestingly, there is a dramatic increase in the red-shift of the Soret bands for the new TBC compounds described here: Soret for **3**, 520 nm; **4**, 526 nm; and **7**, 500 nm. All of these are ∼140 nm red-shifted relative to the analogous phthalocyanine. The Q-bands are blue-shifted by ∼40 nm, which is in accord with the other TBC compounds. The shoulders that appear at shorter wavelengths near the Q-bands of the TBC compounds can be assigned to vibrational bands.

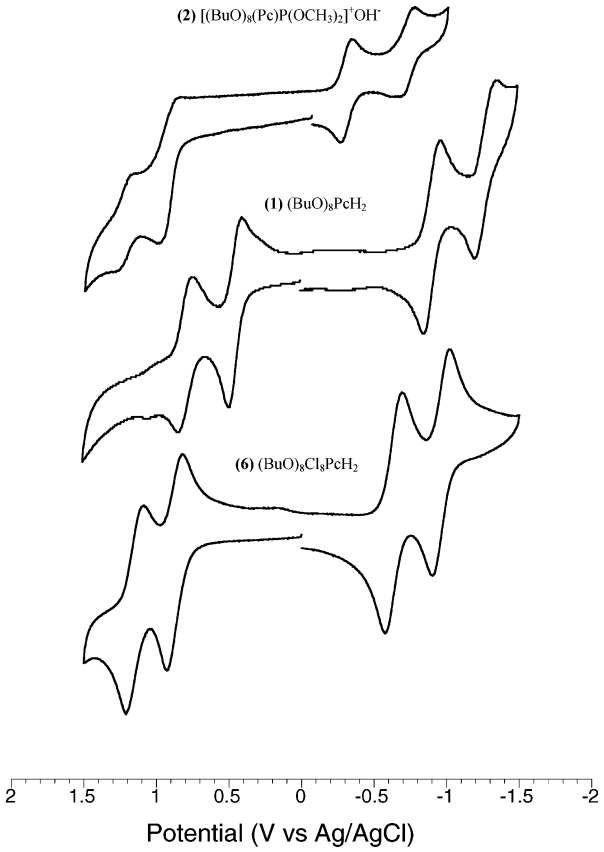

Figure 4. Cyclic voltammograms of compounds **1**, **2**, and **6** in CH_2Cl_2 containing 0.1 M TBAP.

Electrochemistry of $(BuO)_8PcH_2$, $[(BuO)_8PcP(OCH_3)_2]^+OH^-$, and $Cl_8(BuO)_8PcH_2$. The cyclic voltammograms of the three phthalocyanine compounds **1**, **2**, and **6** are shown in Figure 4, and their redox potentials are given in Table 2. The metal-free Pc **1** exhibits two reversible oxidations at 0.79

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Table 2. Half-wave Potentials (V vs Ag/AgCl) of Phthalocyanines $(BuO)_8PcH_2$ (**1**), $[(BuO)_8(Pc)P(OCH_3)_2]^+OH^-$ (**2**), $(BuO)_8Cl_8PcH_2$ (**6**), PcH_2, and $(t\text{-}Bu)_4PcH_2$

	oxidation		reduction		
compd	1st	2nd	1st	2nd	ΔE_{ox-red}[a]
1	0.45	0.79	−0.91	−1.23	1.36
2	0.95	1.24	−0.23	−0.62	1.18
6	0.88	1.15	−0.64	−0.96	1.52
PcH_2[b,c,57]	0.69	-	−0.61	−1.01	1.70
$(t\text{-}Bu)_4PcH_2$[b,d,56]	0.62	0.94	−0.82	−1.19	1.44

[a] ΔE_{ox-red} is given as the difference between the first reduction and first oxidation potentials. [b] Values were converted from V vs SCE to V vs Ag/AgCl via $E_{1/2}(SCE) = E_{1/2}(Ag/AgCl) + 0.045$ V. [c] Data collected in DMF, 0.1 M tetrabutylammonium hexafluorophosphate vs SCE. [d] Data collected in CH_2Cl_2, 0.1 M tetrabutylammonium hexafluorophosphate vs SCE.

V (0.74 V vs SCE) and 0.45 V (0.40 V vs SCE), and two reversible reductions at −0.91 V (−0.96 V vs SCE) and −1.23 V (−1.28 V vs SCE). These potentials can be compared with those reported for unsubstituted PcH_2 (Table 2), in which the first oxidation has been given as 0.64 V (vs SCE), and the first and second reductions given as −0.66 and −1.06 V (vs SCE) in DMF. As expected, the butoxy substituents have an electron-donating effect, making **1** both easier to oxidize and more difficult to reduce than PcH_2.[54] The same trend holds even in comparison to the relatively electron-rich tetraalkyl-substituted $(t\text{-}Bu)_4PcH_2$ (Table 2); the two oxidations for the $(t\text{-}Bu)_4PcH_2$ are ∼150 mV more positive than the respective oxidations seen for **1,** and the two reductions for $(t\text{-}Bu)_4PcH_2$ are more positive than the corresponding reductions observed for **1**. Clearly, the butoxy substituents have the effect of pushing electron density onto the macrocycle. The octachloro-substituted analogue **6** also exhibits two reversible oxidations and two reversible reductions, as shown in Figure 4, and from the redox potentials for **6** given in Table 2, it is clear that the eight chloro substituents have a large electron-withdrawing effect. The first and second oxidations are shifted 430 and 360 mV more positive than those of **1**, respectively, and both reversible reductions occur at a potential 270 mV more positive than those of **1**. Indeed, both the oxidations and second reduction for **6** occur at potentials more positive than the respective waves for the unsubstituted PcH_2. These data suggest that the electron-withdrawing capacity of the chloro substituents overpowers the electron donation of the butoxy groups, and makes the octachloro substituted macrocycle electron-poor in comparison with unsubstituted PcH_2.

An extensive literature exists on the electrochemistry of many main-group phthalocyanines, but phosphorus Pc's, as mentioned earlier, in general are notably absent. It is of some interest, therefore, to compare the electrochemical properties of the phosphorus Pc **2** against those of **1** and **6**. Interestingly, the electrochemistry of **2** is markedly different from **1** and **6**, as seen in Figure 4 and listed in Table 2. The insertion of a phosphorus(V) ion has caused dramatic positive shifts in the redox potentials for **2** compared to **1**, making the phosphorus complex much more difficult to oxidize and easier to reduce than the metal free PcH_2. This effect is to be expected from the insertion of a positively charged ion such as P^V. In fact, a linear correlation has been drawn by Lever for unsubstituted phthalocyanine which relates the redox potentials to the radii/charge ratio of the inserted ion.[55] The small radii/charge ratio of the P^V ion (31 pm/5*z*) in **2** is expected to cause a significant positive shift in the redox potentials based on this correlation.

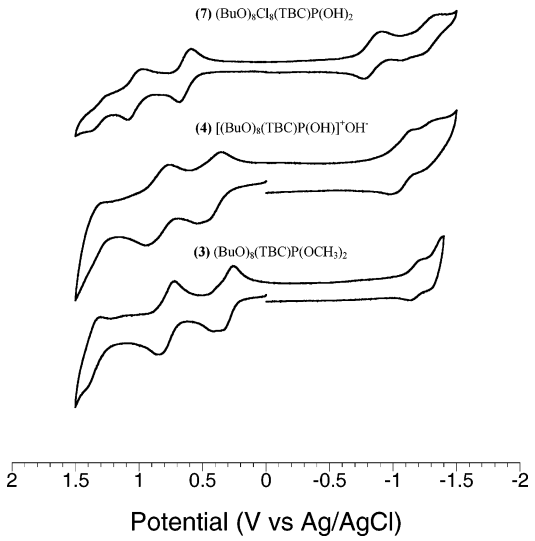

Figure 5. Cyclic voltammograms of compounds **3**, **4**, and **7** in CH_2Cl_2 containing 0.1 M TBAP.

For many porphyrins and phthalocyanines, the first oxidation and first reduction correspond to the removal or addition of an electron from the frontier orbitals of the π system, and the potential difference ($\Delta E_{ox-red} = E_{ox} - E_{red}$) between them is very similar for a given series of compounds, corresponding to the HOMO−LUMO energy gap.[56] For metal-free Pc's, $\Delta E_{ox-red} = 1.4$ V on average,[57] and compounds **1** and **6** conform nicely to this trend (Table 2). However, the small ΔE_{ox-red} value of 1.18 V for **2** is considerably out of the normal range for either metal-free ($\Delta E_{ox-red} = 1.4$ V) or main-group Pc's ($\Delta E_{ox-red} = 1.5$ V).[57] In fact, given the relatively positive value of the first reduction potential for **2**, we suggest that this process is a reduction of phosphorus rather than the ring, or involves a π orbital with significant phosphorus character, and therefore, ΔE_{ox-red} does not correspond to the HOMO−LUMO energy gap of the aromatic π-system.

(b) Electrochemistry of $(BuO)_8(TBC)P(OCH_3)_2$, $[(BuO)_8(TBC)P(OH)]^+OH^-$, and $[(BuO)_8Cl_8(TBC)P(OH)]^+OH^-$. The cyclic voltammograms for **3**, **4**, and **7** are shown in Figure 5, and the corresponding redox potentials are given in Table 3. As seen in Figure 5, the overall electrochemical behavior of the three TBC compounds is similar, with two oxidation waves and one or two reduction waves observed within the solvent window. The difference in axial ligands between **3** and **4** has only a small effect on the redox potentials. As expected, the chlorinated TBC **7** exhibits

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Table 3. Half-wave Potentials (V vs Ag/AgCl) of Triazatetrabenzcorroles $(BuO)_8(TBC)P(OCH_3)_2$ (**3**), $[(BuO)_8(TBC)P(OH)]^+OH^-$ (**4**), and $[(BuO)_8Cl_8(TBC)P(OH)]^+OH^-$ (**7**)

	oxidation		reduction		
compd	1st	2nd	1st	2nd	ΔE_{ox-red}[a]
3	0.32	0.78	−1.16	-	1.48
4	0.42	0.85	−1.08	-	1.50
7	0.64	1.04	−0.85	−1.27	1.49

[a] ΔE_{ox-red} is given as the difference between the 1st reduction and 1st oxidation potentials.

marked positive shifts in both the reduction and oxidation potentials compared to **3** and **4**, in keeping with the expected electron-withdrawing effect of the Cl^- substituents. This effect appears to be large enough to cause a second reduction at −1.22 V to come into view, as opposed to the other TBCs **3** and **4**, which show essentially only one reduction. To our knowledge, the electrochemical properties of a triazatetrabenzcorrole macrocycle have only been reported recently for the silicon complex $TBCSi(OSiEt_3)$.[58] The cyclic voltammogram of this complex is somewhat similar to the TBCs described here, exhibiting two reduction couples at −1.22 and −1.66 (V vs Ag/AgCl) and two oxidation couples at 0.63 and 1.14 (V vs Ag/AgCl). However, the ΔE_{ox-red} = 1.85 V is rather different from the average ΔE_{ox-red} of 1.49 V for compounds **3**, **4**, and **7**. As already discussed, the observed difference between the first reduction and first oxidation for phthalocyanines is $\Delta E_{ox-red} \sim 1.50$ V, which typically corresponds to the HOMO−LUMO gap. Interestingly, the average ΔE_{ox-red} values observed for the triazatetrabenzcorroles examined in this study agree well with this range and suggest this value may represent the HOMO−LUMO gap for the TBCs. The ΔE_{ox-red} value for the Si derivative may not correspond to the HOMO−LUMO gap of the π-system in this particular TBC compound.

The most dramatic effect is observed if one compares the redox potentials for the TBC compounds versus the corresponding phthalocyanines. The Pc **2** and TBC **3** have the same internal metal ion and axial ligation and, therefore, provide a good pair of compounds for direct comparison. The first and second oxidations for TBC **3** are 630 and 460 mV more negative than the corresponding processes for Pc **2**. In addition, the reduction for **3** is several hundred millivolts more negative than both reductions for **2**. These dramatic shifts indicate that TBC **3** is much more electron-rich compared to the analogous Pc molecule. Such a finding is perfectly consistent with the formal 3− charge of the TBC ring $[(TBC(3-)P^V(OMe)_2]$, as compared to the 2− charge of the corresponding Pc, $[Pc(2-)P^V(OCH_3)_2]^+$. However, these differences in redox potential may also be attributed to the difference in overall charge, i.e., a cationic Pc complex versus a neutral TBC complex. In any case, these findings are consistent with the general notion that corroles help stabilize higher oxidation states.

Chemical Oxidation of $[(BuO)_8(TBC)P(OH)]^+OH^-$ (4). The TBC **4** was oxidized by the addition of a stoichiometric amount of $AgNO_3$ to a solution of **4** in toluene/methanol (1/1 v/v) in an EPR tube. An immediate color change was observed from purple to dark green, and the solution was then degassed, placed under argon, and frozen in liquid nitrogen prior to transfer to the EPR instrument. A singlet centered at $g = 2.003$ with a peak-to-trough separation of 13 G is observed. A control EPR spectrum of **4** was taken prior to addition of Ag^+, and no EPR signal was observed. The spectrum is typical of a simple π-cation-radical porphyrinoid species,[59−61] which we assign to the oxidized product $[(BuO)_8(TBC)P(OH)]^{2+}$. Although the site of oxidation in metalloporphyrinoid compounds often can be difficult to assign (ring vs metal), in this case the phosphorus ion is already in the highest accessible oxidation state and the EPR spectrum clearly points to an oxidized ring system. The color of the oxidized product persists for long periods (hours) at room temperature, suggesting that the π-cation radical is quite stable. The formal potential of Ag^+ in CH_2Cl_2 has been given as 0.65 V (vs SCE),[62] which falls conveniently between the first and second oxidation couples for **4** (see Table 3 and Figure 5). Although the chemical oxidation was done in toluene/methanol for EPR measurements, we propose that this π-cation-radical species is the product of the first oxidation seen in the cyclic voltammogram.

Conclusions

In conclusion, we have synthesized a new series of TBC macrocycles based on the octabutoxy-substituted framework. We have shown that, despite the possible difficulties from steric crowding, the 3′,6′-butoxy-substituted Pc's **1** and **6** undergo facile ring contraction to the TBC compounds. It is possible to define the axial ligation of the P^V centers through an examination of the spectroscopic data, especially ^{31}P NMR, in which there is a clear trend in chemical shift with axial ligation state. Examination of UV−vis properties has shown that the TBCs prepared in this study have a dramatically red-shifted Soret band, even more red-shifted than previously characterized TBCs. We have also shown that the insertion of P^V into the Pc **1** leads to an unexpected dramatic red-shift of the Q-band, as seen in the UV−vis for **2**. To our knowledge, this Q-band is the farthest red-shifted Q-band for a Pc molecule reported to date. From cyclic voltammetry, we have demonstrated that the TBCs are easier to oxidize and more difficult to reduce than their Pc counterparts, which is consistent with the notion that corroles, in general, tend to stabilize high oxidation states.

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