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Synthesis and X-ray Crystal Structure of a P-Confused Carbaporphyrinoid

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Summary: The reaction of a phosphole-2,5-diol with a tripyrromethane in the presence of BF_3 generates, after oxidation by DDQ, a P-confused carbaporphyrinoid whose X-ray crystal structure analysis has been performed. The steric bulk of the phosphorus subunit prevents the formation of the expected phosphaporphyrin.

Within the vast porphyrin field, a topic of great interest is the chemistry of heteroporphyrins.[1] Numerous oxa-, thia-, selena-, and telluraporphyrins have been described.[2] Porphycene analogues are also known.[3] Until very recently, phosphaporphyrins remained unknown, when Matano and his group described the first 21-phospha-23-thiaporphyrin.[4] Spectroscopic and theoretical data clearly indicate that the macrocycle is aromatic. Unfortunately, no X-ray crystal structure is available. In parallel with the group of Matano, we have started to study the possible synthetic routes to phosphaporphyrins. Using a completely different approach, we have obtained an unexpected result, on which we report hereafter.

Some time ago, we described a simple method that converts α-unsubstituted into α-functionalized phospholides.[5] This method has been applied, inter alia, to the synthesis of 2,5-diacylphospholides.[6] These results have provided us with the necessary starting point for our first attempts to make a phosphaporphyrin. After optimization, we are now able to get reproducibly the bifunctional phosphole sulfide **1**[7] in a one-pot procedure in 30% overall yield from 3,4-dimethylphospholide without contamination by the monofunctionalized product (Scheme 1).

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(1) Reviews: Latos-Grazynski, L. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. *2*, pp 361−416. Sessler, J. L.; Seidel, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 5134−5175.

(2) Selected references are as follows. Oxygen: Chmielewski, P. J.; Latos-Grazynski, L.; Olmstead, M. M.; Balch A. L. *Chem. Eur. J.* **1997**, *3*, 268−278. Vogel, E.; Haas, W.; Knipp, B.; Lex, J.; Schmickler, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 406−409; Sulfur: Ulman, A.; Manassen, J. *J. Am. Chem. Soc.* **1975**, *97*, 6540−6544. Vogel, E.; Röhrig, P.; Sicken, M.; Knipp, B.; Herrmann, A.; Pohl, M.; Schmickler, H.; Lex, J. *Angew. Chem, Int. Ed. Engl.* **1989**, *28*, 1651−1655. Selenium: Vogel, E.; Fröde, C.; Breihan, A.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed.* **1997**, *36*, 2609−2612; Tellurium: Latos-Grazynski, L.; Pacholska, E.; Chmielewski, P. J.; Olmstead, M.; Balch, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2252−2254.

(3) Oxygen: Vogel, E.; Sicken, M.; Röhrig, P.; Schmickler, H.; Lex, J.; Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 411−414.

(4) Matano, Y.; Nakabuchi, T.; Miyajima, T.; Imahori, H.; Nakano, H. *Org. Lett.* **2006**, *8*, 5713−5716.

(5) Holand, S.; Jeanjean, M.; Mathey, F. *Angew. Chem., Int. Ed.* **1997**, *36*, 98−100.

(6) Toullec, P.; Mathey, F. *Synlett* **2001**, 1977−1979.

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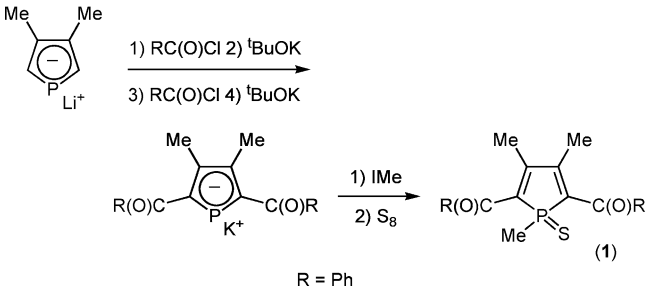
Scheme 1



Whereas the reduction of **1** by $NaBH_4$ alone affords a complex mixture of products, the reduction of **1** by $NaBH_4$/$CeCl_3$ cleanly produces the expected bis-carbinol **2**[8] as a 50:50 mixture of two diastereomers. The *meso* diastereomer displays symmetrical ^{1}H and ^{13}C NMR spectra, whereas the *rac* diastereomer shows two sharply different series of resonances for the methyl and functional groups on the ring carbons. The

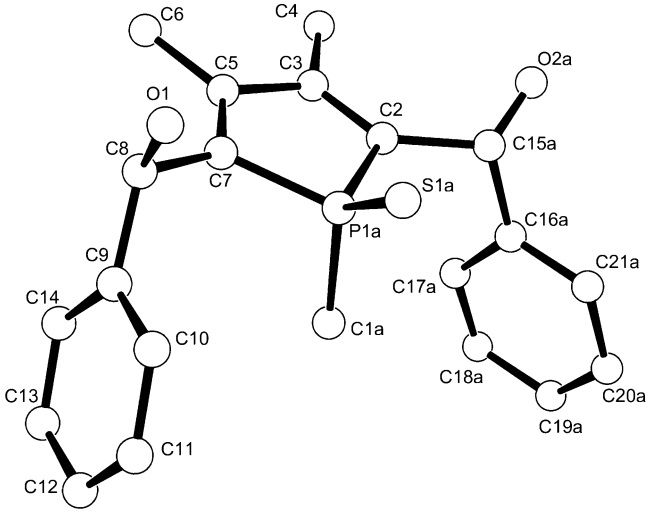
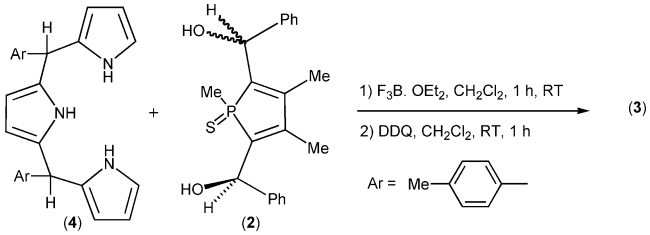


Figure 1. Molecular structure of the *S*,*S* enantiomer of *rac*-**2**. Main bond lengths (Å) and angles (deg): P1−S1 = 2.080(13), P1−C2 = 1.771(9), P1−C7 = 1.796(7), P1−C1 = 1.813(11), C2−C3 = 1.365(8), C2−C15 = 1.551(11), C15−O2 = 1.18(2), C3−C5 = 1.485(8), C5−C7 = 1.349(8), C7−C8 = 1.498(9), C8−O1 = 1.426(7); C2−P1−C7 = 94.3(4), C1−P1−S1 = 118.1(17), P1−C2−C15 = 110.8(7), P1−C7−C8 = 121.9(5).

Scheme 2



X-ray crystal structure analysis of the *rac* isomer (Figure 1)[9−15] shows that the β-methyl substituents block the free rotation of the functional groups. After optimization, the cyclization was performed by reaction of **2** (*rac* + *meso*) with the tripyrromethane **4**,[16] as shown in Scheme 2).

Purification by chromatography on alumina + silica gel with hexane−ether as the eluent yielded, first, traces of the red tetratolylporphyrin identified by exact mass measurement and ^{1}H NMR spectroscopy, followed by a highly stable blue-green solid (**3**)[17] showing a single ^{31}P resonance at 41.9 ppm. We were able to get microcrystals of **3**[18−21] by slow evaporation of dichloromethane solutions. The resulting molecular structure is

(7) **1**: 1-phenyl-3,4-dimethylphosphole (5 g, 26.6 mmol) in dry THF (100 mL) was allowed to react with an excess of lithium wire until the P−Ph bond cleavage was completed (δ(^{31}P) (phospholide) +54.5 ppm). After excess lithium was removed, the solution was treated with *tert*-butyl chloride (3 mL, 26.6 mmol) and heated to 60 °C for 1 h. Benzoyl chloride (3.7 mL, 31.9 mmol) was added dropwise at −78 °C. The mixture was warmed to room temperature and monitored by ^{31}P NMR (observation of several dimers as AB systems). A yellow color was observed upon completion of the reaction. ^{t}BuOK (3 g, 26.6 mmol) was slowly added at 0 °C, and the solution was stirred at 60 °C for 2 h (δ(^{31}P) +150 ppm). Again the same quantity of benzoyl chloride (3.7 mL) was added at −78 °C, then directly an ice bath was used for the addition of ^{t}BuOK (3.5 g, 31.9 mmol), and finally the mixture was directly heated to 60 °C for 2 h (δ(^{31}P) +207 ppm). These additions have to be done as fast as possible to avoid the formation of byproducts. Then iodomethane (1.67 mL, 26.6 mmol) was added via a syringe at −50 °C, and the solution was warmed to room temperature (δ(^{31}P) +10 ppm). Sulfurization was performed by addition of sulfur powder (0.9 g, 28.1 mmol). After vacuum distillation of the solvent, the residue was chromatographed with a mixture of dichloromethane and hexane (70:30) to yield 2.9 g (30%) of yellow crystals. ^{31}P NMR ($CDCl_3$): δ +56.7 ppm. ^{1}H NMR ($CDCl_3$): δ 1.79 (d, ^4J(H−P) = 2.3 Hz, 6H, CH_3); 2.16 (d, ^1J(H−P) = 14.6 Hz, 3H, P−CH_3); 7.37−7.87 (m, 10H, *Ph*). ^{13}C NMR ($CDCl_3$): δ 16.28 (d, ^3J(C−P) = 12.6 Hz, −*C*H$_3$); 20.56 (d, ^1J(C−P) = 51.2 Hz, P−*C*H$_3$); 128.9, 129.6 (s, Ph, $C_{ortho,\ meta}$); 134.1 (s, C_{para}); 137.7 (d, ^1J(C−P) = 70.2 Hz, C_α); 137.6 (s, Ph, C_{ipso}); 150.1 (d, ^2J(C−P) = 19 Hz, C_β); 192.8 (d, ^2J(C−P) = 10.8 Hz, −*C*=O). Mass spectrum (EI, 70 eV): *m/z* 367 (MH^+, 100%).

(8) **2**: cerium(III) chloride heptahydrate (0.45 g, 1.2 mmol) was added to 1,3,4-trimethyl-2,5-dibenzoylphosphole 1-sulfide (0.37 g, 1 mmol) in CH_2Cl_2 (4 mL) and methanol (6 mL). The reaction mixture was cooled to 0 °C, sodium borohydride (0.09 g, 2.4 mmol) was added, and the mixture was then warmed to room temperature for 1 h. After evaporation of the solvents, the residue was chromoatographed with a mixture of dichloromethane and ethyl acetate (95:5) to yield 0.22 g (60%) of **2**. Separation of the diastereomers of **2** can be carried out by chromatography with 60:40 (*meso* isomer) and 50:50 petroleum ether−ether (*rac* isomer). Characterization of the *meso* isomer: ^{31}P NMR ($CDCl_3$) +49 ppm; ^{1}H NMR ($CDCl_3$) δ 0.79 (d, ^2J(H−P) = 14.1 Hz, 3H, P−CH_3), 2.09 (d, J(H−P) = 2.4 Hz, 6H, CH_3), 5.99 (d, ^3J(H−P) = 18.7 Hz, 2H, *H*−C−Ph), 7.23−7.39 (m, 10H, *Ph*); ^{13}C NMR ($CDCl_3$) δ 14.45 (d, ^3J(C−P) = 13.9 Hz, *Me*−C), 19.60 (d, ^1J(C−P) = 49.4 Hz, *Me*−P), 71.79 (d, ^2J(C−P) = 10.1 Hz, *C*−O), 126.12, 127.91, 128.71 (3 s, *C*H (Ph)),135.44 (d, ^1J(C-P) = 77.2 Hz, =*C*H−P), 141.71 (s, C_{ipso} (Ph)), 146.54 (d, ^2J(C−P) = 22.8 Hz, Me−*C*); mass spectrum *m/z* 371 (M + H, 57%), 353 (M − OH, 100%). Characterization of the *rac* isomer: ^{31}P NMR ($CDCl_3$) +50 ppm; ^{1}H NMR ($CDCl_3$) δ 1.34 (d, ^2J(H−P) = 14.1 Hz, 3H, P−CH_3), 1.64 (broad s, 3H, CH_3), 1.95 (d, *J*(H−P) = 2.3 Hz, 3H, CH_3), 5.61 (d, ^3J(H−P) = 9.9 Hz, 1H, *H*−C−Ph), 5.92 (d, ^3J(H−P) = 19.3 Hz, 1H, *H*−C−Ph), 7.19−7.52 (m, 10H, *Ph*); ^{13}C NMR ($CDCl_3$) δ 14.04 (d, ^3J(C−P) = 13.3 Hz, *Me*−C), 14.75 (d, ^3J(C−P) = 14.6 Hz, *Me*−C), 20.32 (d, ^1J(C−P) = 50.6 Hz, *Me*−P), 71.83 (d, ^2J(C−P) = 10.8 Hz, *C*−O), 74.67 (d, ^2J(C−P) = 8.9 Hz, *C*−O), 126.10, 127.76, 128.09, 128.55, 128.63, 129.07 (6 s, *C*H (Ph)), 134.75 (d, ^1J(C−P) = 77.2 Hz, =*C*H−P), 137.20 (d, ^1J(C−P) = 77.2 Hz, =*C*H−P), 142.06, 142.24 (2 s, C_{ipso} (Ph)), 145.57 (d, ^2J(C−P) = 21.5 Hz, Me−*C*), 146.23 (d, ^2J(C−P) = 22.8 Hz, Me−*C*); mass spectrum *m/z* 371 (M + H, 32%), 353 (M − OH, 100%).

(9) Crystal structure determination of compound **2**: a Bruker X8-APEX[10] X-ray diffraction instrument with Mo radiation was used for data collection. All data frames were collected at low temperature (T = 100 K) using an ω, ϕ scan mode (0.3° ω scan width, hemisphere of reflections) and integrated using the Bruker SAINTPLUS software package.[11] The intensity data were corrected for Lorentz−polarization. Absorption corrections were performed using the SADABS program.[12] SIR97[13] was used for direct methods of phase determination and the Bruker SHELXTL software package[14] for structure refinement and difference Fourier maps. Atomic coordinates and isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of two compounds were refined by means of a full-matrix least-squares procedure on F^2. All H atoms were included in the refinement in calculated positions riding on the C atoms. The drawing of the molecule was carried out using Ortep 3.[15] Crystal and structure parameters: size 0.12 × 0.10 × 0.10 mm^3, orthorhombic, space group *Pbca*, a = 15.552(12) Å, b = 10.704(8) Å, c = 22.633(18) Å, α = 90.0°, β = 90.0°, γ = 90.0°, V = 3768(5) Å^3, ρ_{calcd} = 1.306 g/cm^3, Mo radiation (λ = 0.710 73 Å), T = 100(2) K, 12 901 reflections collected, 2302 independent reflections (R_{int} = 0.1422), absorption coefficient μ = 0.268 mm^{-1}; maximum/minimum transmission 0.9742 and 0.9678, 133 parameters were refined and converged at R1 = 0.0735, wR2 = 0.1507, with intensity $I > 2\sigma(I)$.

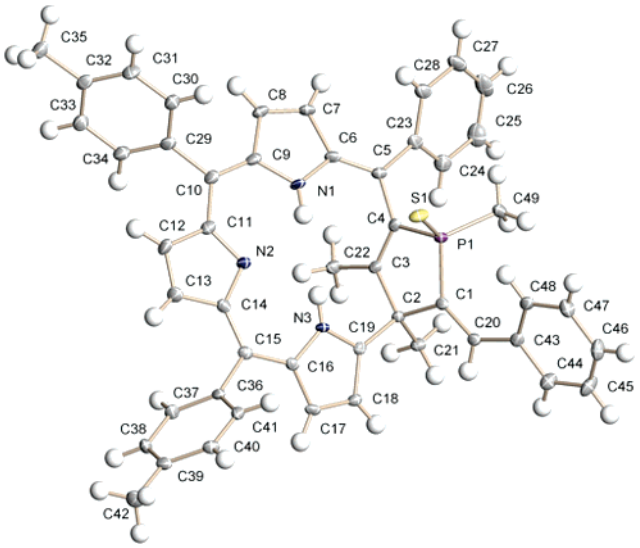
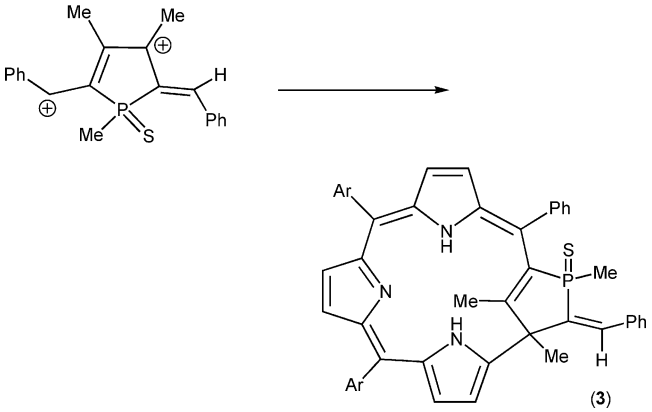


Figure 2. Molecular structure of compound **3**. Main bond lengths (Å) and angles (deg): P1−S1 = 1.9617(9), P1−C49 = 1.807(2), P1−C1 = 1.808(2), P1−C4 = 1.801(2), C1−C2 = 1.560(3), C2−C3 = 1.532(3), C3−C4 = 1.340(3), C1−C20 = 1.343(3), C4−C5 = 1.484(3), C5−C6 = 1.367(3), C6−C7 = 1.459(3), C7−C8 = 1.349(3), C8−C9 = 1.451(3), N1−C6 = 1.389(3), N1−C9 = 1.374(3), N1−H = 0.8800, C9−C10 = 1.378(3), C10−C11 = 1.442(3), C11−C12 = 1.453(3), C12−C13 = 1.347(3), C13−C14 = 1.446(3), C11−N2 = 1.350(3), N2−C14 = 1.404(3), C14−C15 = 1.386(3), C15−C16 = 1.429(3), C16−C17 = 1.395(3), C17−C18 = 1.400(3), C18−C19 = 1.397(3), C16−N3 = 1.381(3), N3−C19 = 1.356(3), C19−C2 = 1.513(3); C1−P1−C4 = 93.45(10), C2−C3−C4 = 117.46(19), C3−C4−C5 = 126.3(2), C4−C5−C6 = 120.1(2), C6−N1−C9 = 112.20(18), N1−C9−C10 = 125.5-(2), C9−C10−C11 = 123.2(2), C10−C11−N2 = 125.1(2), C11−N2−C14 = 105.30(18), N2−C14−C15 = 125.4(2), C14−C15−C16 = 124.2(2), C15−C16−N3 = 122.28(19), C16−N3−C19 = 110.81(18), N3−C19−C2 = 121.72(19), C19−C2−C3 = 110.27-(17).

Scheme 3



shown in Figure 2). **3** is an isomer of the dihydrophosphaporphyrin in which the phosphorus atom lies outside of the central

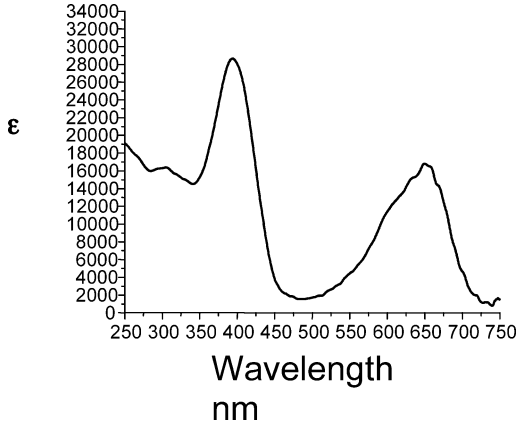


Figure 3. UV−vis absorption spectrum of **3** in EtOH−CH_2Cl_2 (50:50).

hole. Its structure is related to the X-confused carbaporphyrinoids.[22] The three pyrrole nuclei display very different structural parameters. The N1 ring shows two $C_\alpha-C_\beta$ single bonds at 1.459(3) and 1.451(3) Å and one $C_\beta-C_\beta$ double bond

(10) APEX 2, version 2.0-2; Bruker AXS Inc., Madison, WI, 2005.
(11) SAINT, version V7.21A; Bruker AXS Inc., Madison, WI, 2005..
(12) SADABS, version 2004/1; Bruker Analytical X-Ray Systems, Inc., Madison, WI, 2004.
(13) Altomare, A.; Burla, M. C.; Carnalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR 97. *J. Appl. Crystallogr.* **1999**, *32*, 115−122.
(14) SHELXTL Software, Version 6.14, Dec; Bruker Analytical X-Ray Systems, Inc., Madison, WI, 2003..
(15) ORTEP3 for Windows: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
(16) Ka, J.-W.; Lee, C.-H. *Tetrahedron Lett.* **2000**, *41*, 4609−4613.
(17) In a Schlenk, $BF_3{\cdot}OEt_2$ (7 μL, 0.028 mmol) was added at once to a solution containing the tripyrromethane **4** (58.6 mg, 0.14 mmol), bis-(carbinol) **2** (51.8 mg, 0.14 mmol), and CH_2Cl_2 (0.5 mL). The resulting dark "paste" was redissolved in CH_2Cl_2 (1 mL) and stirred while being protected from solar light for 1 h. Then DDQ (47.6 mg, 0.2 mmol) was added to the reaction mixture and stirred again for 1 h. The product was directly purified by chromatography on silica gel, with some alumina on the top of the column to retain most of the polymers. Eluent: hexane−ether (70:30). Yield: 2 mg (2%) of **3**. ^{31}P NMR (CD_2Cl_2): +41.9 ppm. ^{1}H NMR (CD_2Cl_2): δ 1.20 (d, ^2J(H−P) = 13.5 Hz, 3H, P−CH_3), 1.28 (s, 3H, −C$_\beta$−CH_3), 1.55 (br, 2H, NH), 2.19 (s, 3H, P−C=C$_\beta$−CH_3), 2.44 and 2.46 (2s, 3 + 3H, C_6H_4−CH_3), 7.16−7.81 (m, 27H, =C−*H*, *Ph*, *Pyr*, C_6H_4). ^{13}C NMR (CD_2Cl_2): δ 14.69 (s, *C*H_3−C(sp^3)), 21.53 and 21.63 (2 s, *C*H_3 tolyl), *C*H_3−P masked by the tolyl *C*H_3 (as shown by the ^{1}H−^{13}C correlation data), 25.66 (s, *C*H_3−C(sp^2)), 30.28 (s, *C*(sp^3)), 109.77−144.94 (aromatic *C*). HR-FAB-MS spectrum: *m/z* 736.292 300 (calcd for $C_{49}H_{43}N_3PS$ 736.291 534). UV/vis spectrum: (EtOH/CH_2Cl_2): λ_{max} (ϵ) 392 (2.86×10^4), 651 nm (1.68×10^4).
(18) Crystal structure determination of compound **3**: a black needlelike crystal (0.040 × 0.008 × 0.003 mm) was placed on the tip of an ultrathin glass fiber and mounted on a Bruker SMART6000 platform-CCD three-circle diffractometer. Data collection was carried out using synchrotron radiation (λ = 0.495 95 Å, diamond 111 monochromators, two mirrors to exclude higher harmonics, 5 s/frame exposure time, detector−crystal distance of 6.0 cm, and low temperature at 95(2) K). A randomly oriented region of reciprocal space was surveyed to the extent of two hemispheres. Two major sections of frames were collected with 0.30° steps in θ and ϕ with a detector position of 0° in 2θ. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from 2756 strong reflections from the actual data collection after integration (SAINT).[11] Intensity data were corrected for absorption (SADABS).[19] Refer to ref 9 for additional crystal and refinement information. Structure solution and refinement: the space group $P2_1/c$ was determined on the basis of intensity statistics and systematic absences. The structure was solved using Sir2004[20] and refined with SHELXL-97.[21] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the *E*-map. With subsequent full-matrix least-squares/difference Fourier cycles of refinement, all of the non-hydrogen atoms were identified and their positions refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with individual relative isotropic displacement parameters. The refinement converged at R1 = 0.0497 and wR2 = 0.0946 with intensity $I > 2\sigma(I)$. There was one molecule of $C_{49}H_{42}N_3PS$ present in the asymmetric unit of the unit cell. Cambridge Crystallographic Database files CCDC 630394 and 630395 contain the supplementary crystallographic data for this paper.
(19) An empirical correction for absorption anisotropy, Blessing, R. *Acta Cryst. A* **1995**, *51*, 33−38.
(20) Burla, M. C.; Caliandro, R.; Carnalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. Sir2004, A Program for Automatic Solution and Refinement of Crystal Structure, version 1.0, 2004.
(21) SHELXTL-Plus (current version); Bruker Analytical X-Ray Systems, Madison, WI.

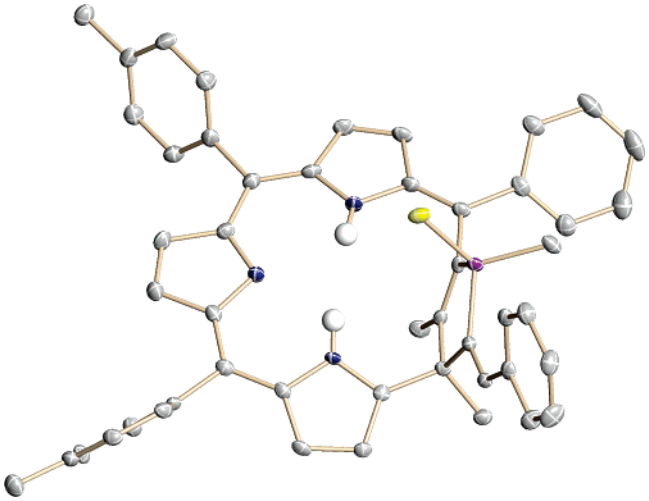


Figure 4. Side view of **3**. Hydrogen atoms (except NH) are omitted for clarity.

at 1.349(3) Å, the N2 ring contains one N═C double bond at 1.350(3) Å, one N−C single bond at 1.404(3) Å, and one C_β−C_β double bond at 1.347(3) Å, and the N3 ring is highly delocalized with three almost equal C−C bond lengths at 1.395(3), 1.400(3), and 1.397(3) Å. The formation of **3** is easily rationalized, as shown in Scheme 3). The nonaromaticity of the phosphole nucleus allows the delocalization of the carbenium positive charge onto the β-carbons of the ring.

(22) Furuta, H.; Maeda, H.; Osuka, A. *Chem. Commun.* **2002**, 1795−1804. For a leading reference on carbaporphyrin, see: Lash, T. D.; Hayes, M. J.; Spence, J. D.; Muckey, M. A.; Ferrence, G. M.; Szczepura, L. F. *J. Org. Chem.* **2002**, *67*, 4860−4874.

Since the macrocycle is nonaromatic, its UV−vis absorption spectrum does not display a Soret band and is quite different from that of a normal porphyrin (Figure 3). The question is why the cyclization produces the nonaromatic reduced isomer **3** rather than the expected aromatic phosphaporphyrin. The side view of **3** (Figure 4) provides a possible answer. The disruption of the electronic delocalization within **3** allows the phosphole ring to rotate away from the mean plane of the pyrrole rings and to suppress the steric crowding inside the central hole. The corresponding tilt angle is 107.6°. Thanks to its two NH bonds and to the *endo* disposition of its P═S bond, **3** can probably act as a dianionic tetradentate ligand toward a single transition-metal center as does a normal porphyrin, but with an entirely different coordination geometry. The corresponding chemistry will be obviously very different from the chemistry of normal porphyrins.

Acknowledgment. We thank Dr. Victor G. Young, Jr., at the University of Minnesota for data collection and structure solution using synchrotron radiation at the ChemMatCARS beamline, Advanced Photon Source, Argonne National Laboratory, Chicago, IL, utilizing the SCrAPS program. ChemMatCARS Sector 15 is principally supported by the National Science Foundation/Department of Energy under Grant No. CHE0087817. The Advanced Photon Source is supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. We thank also Dr. R. O. Al-Kaysi for the recording of the UV−vis spectrum.

Supporting Information Available: CIF files giving X-ray crystal structure analyses of compounds *rac*-**2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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