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Phosphonium Ylides from Nucleophilic Addition of Triphenylphosphine to [26]Hexaphyrin(1.1.1.1.1.1)

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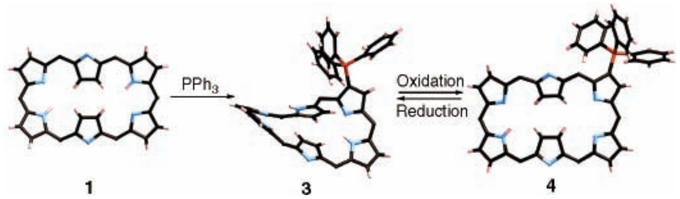
ABSTRACT



Nucleophilic addition of triphenylphosphine to neutral *meso*-hexakis(pentafluorophenyl)-substituted [26]hexaphyrin(1.1.1.1.1.1) (1) provided a stable phosphonium ylide of [28]hexaphyrin (3), which was quantitatively oxidized to its 26π-counterpart (4) that exhibited a planar and rectangular conformation and a diatropic ring current.

Considerable progress has been made in recent years in the search for new expanded porphyrins that display optical, electrochemical, and coordination properties, which are different from those of porphyrins.[1,2] Despite these efforts, the chemistry of expanded porphyrins has still remained quite undeveloped, which may be appreciated by the very limited number of the reported chemical transformations and the lack of consensus for their chemical reactivity. New transformations of expanded porphyrins are highly desirable for the future development of this class of molecules. Along this line, we have been focusing on *meso*-hexakis(pentafluorophenyl) substituted [26]hexaphyrin-(1.1.1.1.1.1) (**1**) as a representative *meso*-aryl-substituted expanded porphyrin.[3] Metalation of **1** has been shown to lead to diverse metal complexes, including bis-copper complexes with gable shapes,[4] group 10 metals (nickel, palladium, and platinum) with distorted structures,[5] and an all-in-plane bis-gold complex that can be switched between aromatic and anti-aromatic, depending upon the number of π-electrons.[6] By contrast, its chemical reactivity has been studied poorly except for a few reports.[7]

It has been reported that π-cation radicals of metalloporphyrins generated by chemical or electrochemical oxidation react with triphenylphosphine to produce corresponding phosphonium adducts.[8] To the best of our knowledge, no

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[2] (a) Vogel, E.; Michels, M.; Zander, L.; Lex, J.; Tuzun, S.; Houk, K. N. *Angew. Chem., Int. Ed*. **2003**, *42*, 2857. (b) Tanaka, Y.; Hoshino, W.; Shimizu, S.; Youfu, K.; Aratani, N.; Maruyama, N.; Fujita, S.; Osuka, A. *J. Am. Chem. Soc*. **2004**, *126*, 3046.

[3] (a) Neves, M. G. P. M. S.; Martins, R. M.; Tomé, A. C.; Silvestre, A. J. D.; Silva, A. M. S.; Felix, V.; Drew, M. G. B.; Cavaleiro, J. A. S. *Chem. Commun*. **1999**, 385. (b) Shin, J.-Y.; Furuta, H.; Yoza, K.; Igarashi, S.; Osuka, A. *J. Am. Chem. Soc*. **2001**, *123*, 7190. (c) Suzuki, M.; Osuka, A. *Org. Lett*. **2003**, *5*, 3943.

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[5] Mori, S.; Shimizu, S.; Taniguchi, R.; Osuka, A. *Inorg. Chem*. **2005**, *44*, 4127.

[6] Mori, S.; Osuka, A. *J. Am. Chem. Soc*. **2005**, *127*, 8030.

[7] (a) Suzuki, M.; Shimizu, S.; Shin, J.-Y.; Osuka, A. *Tetrahedron Lett*. **2003**, *44*, 4597. (b) Suzuki, M.; Taniguchi, R.; Osuka, A. *Chem. Commun*. **2004**, 2682. (c) Hata, H.; Shinokubo, H.; Osuka, A. *Angew. Chem., Int. Ed*. **2005**, *44*, 932. (d) Suzuki, M.; Osuka, A. *Chem. Commun*. **2005**, 3685.

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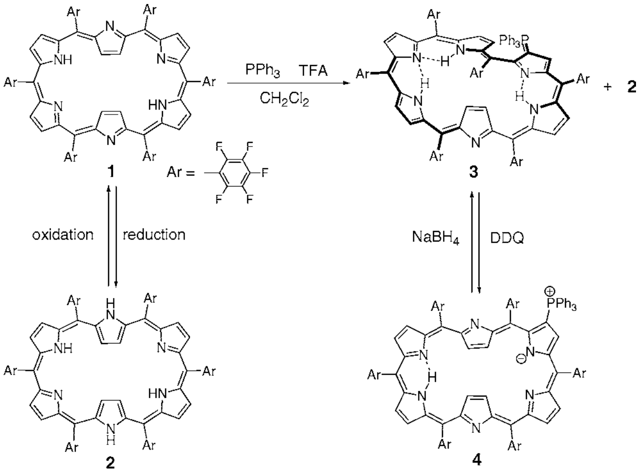
such reaction has been reported between triphenylphosphine and neutral porphyrins. In this paper, we report a facile addition reaction of triphenylphosphine to *meso*-pentafluorophenyl substituted [26]hexaphyrin(1.1.1.1.1.1) **1** that proceeds even in its neutral form to provide a stable phosphonium ylide.

Scheme 1



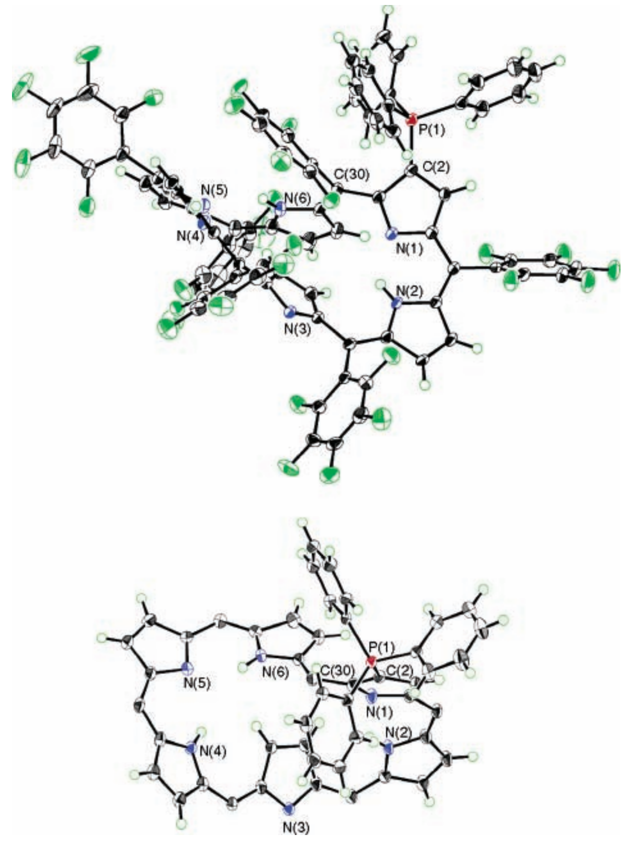


Figure 1. X-ray crystal structure of **3**: (top) top view and (bottom) side view. Thermal ellipsoids are scaled to the 50% probability level. In the side view, *meso*-pentafluorophenyl substituents are omitted for clarity.

An addition of triphenylphosphine to a solution of **1** in CH_2Cl_2 at room temperature caused irreversible changes, as revealed by TLC and MALDI-TOF mass analyses. Allowing the reaction to proceed for 24 h and evaporation of the solvent resulted in a color change from the violet color of the solution to the metallic green color of the residue. Purification by silica gel column chromatography provided **3** as dark blue solids in 80% yield along with a small amount of reduced [28]hexaphyrin **2** (ca. 3−4%) (Scheme 1). The reaction was considerably accelerated in the presence of trifluoroacetic acid (TFA), under which conditions the reaction was completed within 1 h. The product **3** exhibits its parent ion peak at $m/z = 1723.1773$ (calcd for $C_{84}H_{30}N_6F_{30}P$ $[M + H]^+$, 1723.1785) in the ESI-TOF-mass spectrum, in line with its formulation as a triphenylphosphine-adduct of **1**. The structure of **3** has been elucidated by single-crystal X-ray diffraction analysis to be not a phosphonium adduct reported for the reaction of porphyrins but a phosphonium ylide with a rather distorted structure (Figure 1).[9] The triphenylphosphine moiety is bound to the peripheral β-position of hexaphyrin with a P(1)−C(2) bond of 1.751(4) Å, which is shorter than that of β-triphenylphosphine substituted iron(III)-porphyrin (1.799(9) Å) complex[8c] but slightly longer than those of phosphonium ylides (1.63−1.73 Å),[10] suggesting a single bond and double bond mixed character. Importantly, no counteranion was found around the phosphorus atom, supporting the phosphonium ylide structure for **3**. One of the phenyl groups of the triphenylphosphine moiety is arranged parallel with the *meso*-pentafluorophenyl substituent at C(30) with an interplanar distance of 3.55 Å, probably due to favorable phenyl-pentafluorophenyl stacking interaction,[11] and there are hydrogen bonding interactions between N(6)H and N(5) (N(6)•••N(5), 2.66 Å) and N(4)H and N(5) (N(4)•••N(5), 2.82 Å). Such intramolecular interactions are likely to induce the distorted structure. In the ^1H NMR spectrum taken at room temperature, only two NH signals were observed at 8.20 and 9.07 ppm, while another NH signal was detected at 6.56 ppm at 0 °C. Eleven signals due to the β-protons were observed in the range of 3.20−7.57 ppm. These ^1H NMR data indicated the absence of a diatropic ring current for **3**. A peak at 12.87 ppm in the ^{31}P

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(8) (a) Shine, H. J.; Padilla, A. G.; Wu, S. M. *J. Org. Chem.* **1979**, *44*, 4069. (b) Smith, K. M.; Barnett, G. H.; Evans, B.; Martynenko, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5953. (c) Maąek, A.; Latos-Grażyński, L.; Bartczak T. J.; Ządło, A. *Inorg. Chem.* **1991**, *30*, 3222. (d) Rachlewicz, K.; Latos-Grażyński, L. *Inorg. Chem.* **1995**, *34*, 718. (e) Ruhilmaa, L.; Giraudeau, A. *Chem. Commun.* **1996**, 2007. (f) Ruhlmann, L.; Giraudeau, A. *Eur. J. Inorg. Chem.* **2001**, 659. (g) Ruhlmann, L.; Gross, M.; Giraudeau, A. *Chem. Eur. J.* **2003**, *9*, 5085.

(9) **Crystal data for 3:** $C_{88}H_{29}N_6F_{30}P$, $0.66(C_8H_{18})$, $0.34(CH_2Cl_2)$, H_2O; formula wt 1928.29, $T = 90(2)$ K, monoclinic, $P2_1/c$ (No. 14), $a = 14.589(6)$, $b = 21.295(9)$, $c = 26.237(11)$ Å, $\beta = 98.157(7)°$, $V = 8069(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.587$ g cm^{-3}, μ(Mo Kα) = 0.247 mm^{-1}, $F(000) = 3871.4$, 47627 reflections measured, 18230 unique, $R1 = 0.0874$, $wR2 = 0.2420$, GOF = 1.430 ($I > 2.0\sigma(I)$). CCDC file no. 277896.

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NMR spectrum confirmed the substitution of triphenylphosphine group to hexaphyrin.

Further, the adduct **3** was oxidized with iodine or DDQ to give **4** as blue solids quantitatively (Scheme 1). In the isolation of **4**, it is crucial to wash the product thoroughly with aqueous NaOAc solution, since it is quite easily protonated. Single crystals of **4** were obtained by slow diffusion of octane to its chloroform solution. The X-ray structure of **4** shows a planar and rectangular macrocyclic shape with dome-like ruffling (Figure 2).[12] The mean plane deviation defined by the constitutional 30 atoms is 0.350 Å. As is the case for **3**, one of the phenyl groups in the triphenylphosphine moiety is arranged parallel with the pentafluorophenyl group at C(30), probably through phenyl-pentafluorophenyl stacking interaction. Absence of any counteranion around the phosphorus atom again supported the phosphonium ylide structure for **4**. More importantly, the bond length of P(1)−C(2) in **4** is 1.763(6) Å, which is distinctly longer than that of **3** but again in a range between the single bond and double bond. The compound **4** exhibits its parent ion peak at $m/z = 1721.1668$ (calcd for $C_{84}H_{28}N_6F_{30}P$ $[M + H]^+$, 1721.1629) in the ESI-TOF-mass spectrum. The ^1H NMR spectrum of **4** exhibits the inner β-protons in the shielded region at 0.40, 0.13, −0.03, and −0.75 ppm, and the outer β-protons in the deshielded region in the range of 8.90−7.95 ppm, hence indicating a strong diatropic ring current in line with its 26π-aromatic conjugation as in the parent hexaphyrin **1**. The ^{31}P NMR spectrum of **4** showed a singlet at 14.74 ppm.

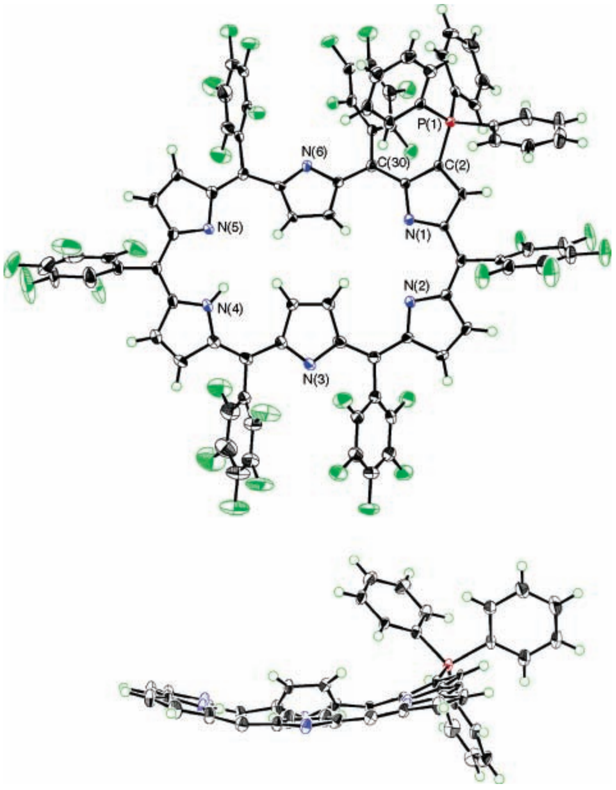

Figure 2. X-ray crystal structure of **4**: (top) top view and (bottom) side view. Thermal ellipsoids are scaled to the 50% probability level. In the side view, *meso*-pentafluorophenyl substituents are omitted for clarity

Generally, phosphonium ylides are considered to be a resonance hybrid between a dipolar form and a double bond form. Relative contribution of each resonance hybrid must depend on structural and electronic factors. Figure 3 compares the absorption spectra of **1**, **3**, and **4**. The [28]-hexaphyrin ylide **3** shows ill-defined Soret-like bands at 466 and 631 nm and red-shifted and intensified Q-like band at 1053 nm, whereas the [26]hexaphyrin ylide **4** exhibits an absorption spectrum similar to that of **1**, featuring a distinct Soret-like band at 597 nm, which is slightly broader and 30 nm red-shifted compared with that of **1**. The marked difference in the spectral feature between **3** and **4** may be explained in terms of the number of π-electrons in the circuit as well as different contribution of the resonance hybrid. Double bond forms such as **3A** and **4A** lead to cross conjugation, which is unfavorable for the overall effective conjugation of hexaphyrin (Scheme 2). On the other hand, dipolar canonical forms, represented by **4B**, are favorable for the overall 26π-conjugation in its flat structure, which leads to the aromatic character and diatropic ring current. Therefore, the observed diatropic ring current for **4** suggests dominant contribution of dipolar forms in **4** compared with that in **3**, which seems consistent with the longer C−P bond distance in **4** compared with that in **3**. Finally, these hexaphyrin ylides **3** and **4** were found so stable not to undergo any Wittig-type reactions with aldehydes.

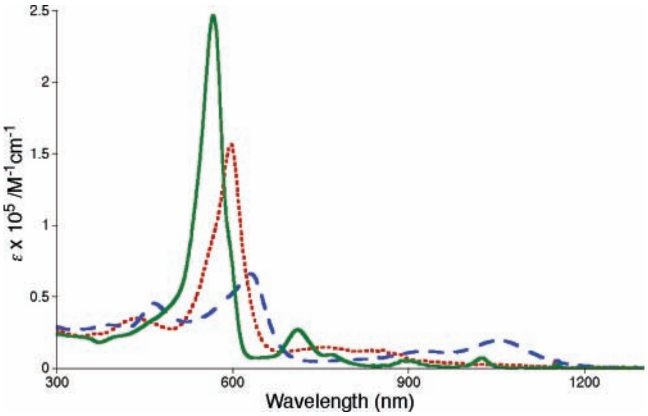

Figure 3. UV−vis absorption spectra of **1** (green, solid line), **3** (blue, dashed line), and **4** (red, dotted line) in $CHCl_3$.

In contrast to the reaction of the neutral form of **1** with triphenylphosphine, 5,10,15,20-tetrakis(pentafluorophenyl)-

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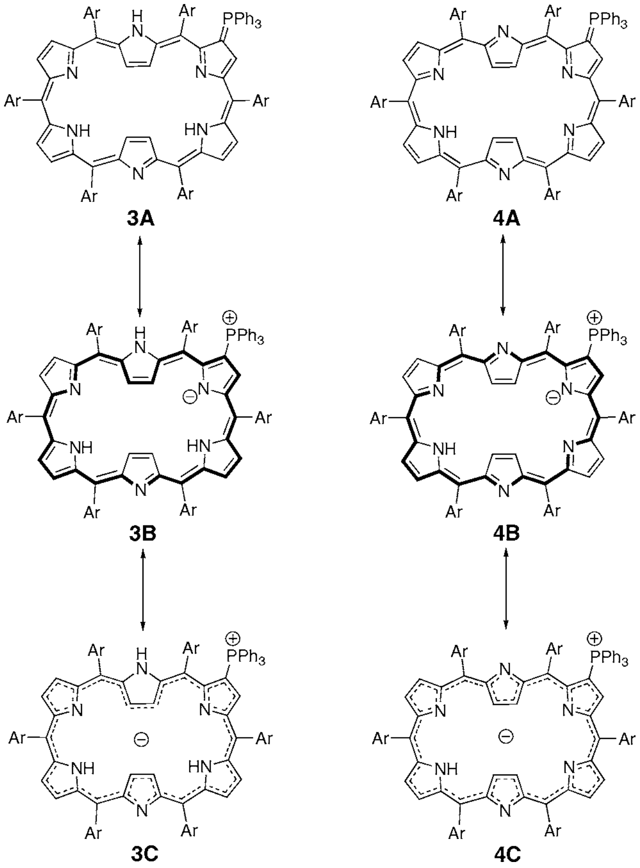
(12) **Crystal data for 4:** $2(C_{84}H_{27}N_6F_{30}P)$, C_8H_{18}, $9(CHCl_3)$; formula wt 4630.71, $T = 90(2)$ K, triclinic, P-1 (No. 2), $a = 15.337(5)$, $b = 16.233(5)$, $c = 20.665(6)$ Å, $\alpha = 74.219(5)$, $\beta = 78.531(6)$, $\gamma = 65.220(5)°$, $V = 4474(2)$ Å^3, $Z = 1$, $D_{calcd} = 1.719$ g cm^{-3}, μ(Mo Kα) = 0.551 mm^{-1}, $F(000) = 2304$, 23160 reflections measured, 15493 unique, $R1 = 0.0977$, $wR2 = 0.2668$, GOF = 1.039 ($I > 2.0\sigma(I)$). CCDC file no. 277897.

Scheme 2. Possible Resonance Structures of **3** and **4**



porphyrin **5** did not react. One possible reason may be much stronger oxidizing power of **1** compared with that of **5**. In accord with this consideration, the [26]hexaphyrin **1** undergoes two reversible one-electron reductions at −0.52 and −0.85 V in CH_2Cl_2 versus ferrocene/ferrocenium ion couple with tetrabutylammonium tetrafluoroborate electrolyte,[6] whereas the porphyrin **5** shows two reduction peaks at −1.28 and −1.71 V.[13] As such, [28]hexaphyrin(1.1.1.1.1.1) reduced form **2** did not react with triphenylphosphine under the same conditions. The observed accelerating effect of TFA may be understood in terms of its effective protonation of **1**, hence enhancing its electron-deficient property. This consideration may be applied to new reactions of **1** with other nucleophiles. Along this line, we preliminarily found nucleophilic reactions with chloride and bromide ions and an acetate ion, which will be reported elsewhere.

In summary, a facile nucleophilic addition reaction of triphenylphosphine to [26]hexaphyrin **1** to afford the 28π hexaphyrin ylide **3** is described. The 28π-nonaromatic ylide **3** was quantitatively oxidized to the 26π-electronic aromatic ylide **4**, which exhibits a planar and rectangular structure and a diatropic ring current, probably through larger contribution of the dipolar form in the ylide resonance hybrid.

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Supporting Information Available: Synthetic details, characterization data, and single-crystal X-ray data of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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