

Photoinduced Axial Bond Exchange Reaction of Dichlorophosphorus(v)tetraphenylporphyrin Chloride: Photochemical Activation of Central Three-centre Four-electron Bond through the σ - π Interaction

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A novel photoinduced axial bond exchange reaction of dichlorophosphorus(v)tetraphenylporphyrin chloride in various alcohols affords axial dialkoxyphosphorus(v)tetraphenylporphyrin derivatives.

Phosphorus(v)porphyrin, with a six-coordinated phosphorus, is not only a unique nonmetal porphyrin¹ but also an unusual hypervalent phosphorus compound (12-P-6) with a large π -electron system.² Although the photochemical properties of the axial hypervalent bond of the phosphorus(v)porphyrin is an attractive subject in this regard, previous researches focusing on the redox chemistry,³ the structure,⁴ the coordination⁵ and the application⁶ have not considered the photochemical properties. In this paper, we report the photochemical activation of the axial three-centre four-electron (3c-4e) bond of dichlorophosphorus(v)tetraphenylporphyrin chloride in various alcohols, which affords axial dialkoxyphosphorus(v)tetraphenylporphyrin derivatives with stable P-O-R bonds.

The dichlorophosphorus(v)tetraphenylporphyrin chloride **1** was synthesized and crystallized according to the reported procedure.^{3b} The compound **1** was dissolved in a series of dried alcohols (methanol, ethanol and propan-2-ol) and was photoirradiated with a 500 W xenon lamp through UV and IR cut-off filters (Toshiba, L39 and IR25S) water jacketed at room temperature under an argon atmosphere. The UV-VIS absorption spectroscopic changes of **1** in methanol during the steady-state photoirradiation is shown in Fig. 1. After photoirradiation, the absorption peaks of **1** were not observed whereas new absorption peaks were seen at shorter wavelengths. The photoreaction was complete with 3 min, at which point the final absorption spectrum was coincident with that of a typical dialkoxyphosphorus(v) porphyrin.⁵ The product with the blue-shifted absorption showed the ¹H NMR spectra of peripheral protons (pyrrole- β : δ 9.08, d, 8H; phenyl: 7.7-8.0, m, 20H) and a characteristic signal at δ -1.85 (CH₃: d, J_{PH} 26 Hz, 6H) assigned to methoxy protons. The J_{PH} coupling and the strong ring current shift of the methoxy protons imply that the methoxy groups are attached to the central phosphorus atom. The integrated intensities indicate that there are two equivalent methoxy groups per one phosphorus porphyrin moiety. Consequently, it is concluded that the product in methanol is dimethoxyphosphorus(v)tetraphenylporphyrin chloride⁵ which is disubstituted as shown in Scheme 1. For the photoreactions in ethanol and isopropanol, UV-VIS absorption spectroscopic changes are similar to that in Fig. 1 and the products were also assigned to the

corresponding dialkoxyphosphorus(v)porphyrin derivatives.[†] It is noteworthy that the reaction rates of the exchange are much faster than the thermal reactions,⁵ and that **1** is quantitatively converted into the corresponding dialkoxyphosphorus(v)porphyrin derivatives by the photoreaction.

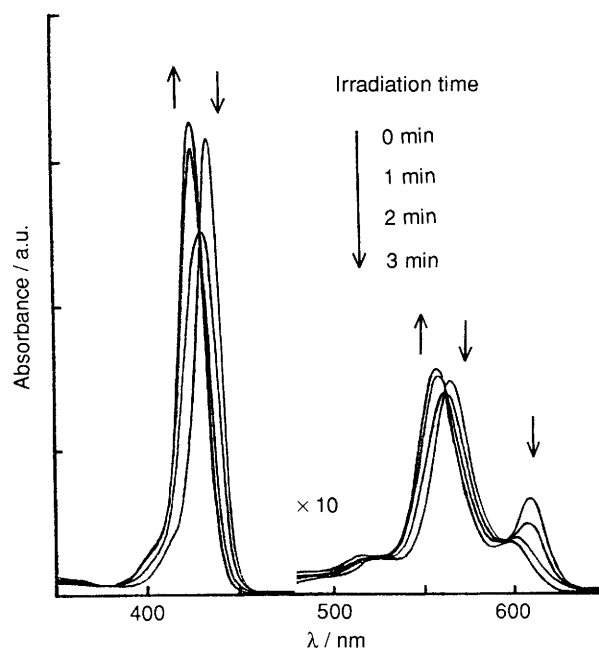
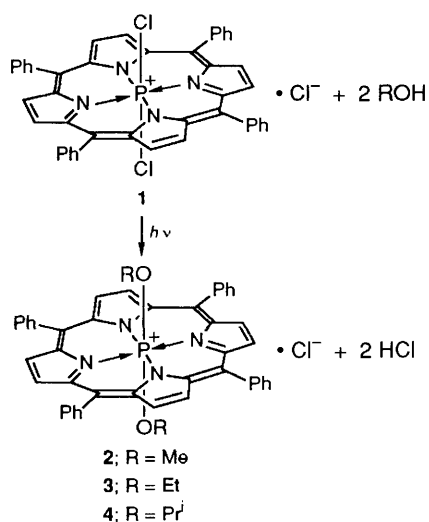


Fig. 1 Absorption spectroscopic changes due to the photoinduced axial bond exchange reaction of dichlorophosphorus(v)tetraphenylporphyrin chloride in methanol

[†] ¹H NMR data of the products (δ rel. to SiMe₄) **2**: δ 9.08 (d, 8H, pyrrole- β), 7.7-8.0 (m, 20H, phenyl), -1.85 (d, 6H, CH₃); **3**: 9.07 (d, 8H, pyrrole- β), 7.7-8.0 (m, 20H, phenyl), -1.73 (dt, 6H, CH₃), -2.34 (dq, 4H, CH₂); **4**: 9.14 (d, 8H, pyrrole- β), 7.8-8.1 (m, 20H, phenyl), -2.19 (d, 12H, CH₃), -2.72 (m, 2H, CH). The products **2-4** have normal-type porphyrin absorption spectra (**2**: 430, 560, 602; **3**: 431, 560, 602; **4**: 426, 552, 593 nm in CHCl₃).



Scheme 1

An interesting feature of the photoinduced axial bond exchange reaction is that monosubstituted phosphorus porphyrin with one alkoxy group was not observed as an intermediate but the disubstituted phosphorus porphyrin was directly obtained. These results are closely related to those for the thermal exchange reactions, *i.e.* the monosubstituted phosphorus porphyrin was not obtained as a stable product but only the disubstituted phosphorus porphyrin was selectively obtained even when the starting compound **1** remained.⁵ We believe that the results are typical feature of the three-centre four-electron (3c-4e) bond composed of Cl-P-Cl along the central axis, in which two Cl are connected to P by the single orbital and could be simultaneously activated by the photochemical and the thermal processes.

The present photoinduced axial bond exchange reaction is important not only for the photochemistry of phosphorus(v) porphyrin but also for the σ - π interaction of hypervalent

phosphorus compound with a large π -electron system.[‡] We are also examining the photochemical hybridization of the phosphorus(v)porphyrins with functional groups toward the axial direction.

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References

- 1 P. Sayer, M. Gouterman and C. R. Connell, *Acc. Chem. Res.*, 1982, **15**, 73; P. Sayer, M. Gouterman and C. R. Connell, *J. Am. Chem. Soc.*, 1977, **99**, 1082; C. J. Carrano and M. Tsutsui, *J. Coord. Chem.*, 1977, **7**, 79; M. Gouterman, P. Sayer, E. Shankland and J. P. Smith, *Inorg. Chem.*, 1981, **20**, 87.
- 2 L. E. Carpenter II and J. G. Verkade, *J. Am. Chem. Soc.*, 1985, **107**, 7084; G. Trinquier, J.-P. Daudey, G. Caruana and Y. Madaule, *J. Am. Chem. Soc.*, 1984, **106**, 4794; R. G. Cavell, K. I. The and L. V. Griend, *Inorg. Chem.*, 1981, **20**, 3813.
- 3 (a) C. A. Marrese and C. J. Carrano, *J. Chem. Soc., Chem. Commun.*, 1982, 1279; (b) *Inorg. Chem.*, 1983, **22**, 1858; (c) 1984, **23**, 3961.
- 4 S. Mangani, E. F. Meyer Jr., D. L. Cullen, M. Tsutsui and C. J. Carrano, *Inorg. Chem.*, 1983, **22**, 400.
- 5 H. Segawa, K. Kunimoto, A. Nakamoto and T. Shimidzu, *J. Chem. Soc., Perkin Trans. 1*, 1992, 939.
- 6 H. Segawa, N. Nakayama and T. Shimidzu, *J. Chem. Soc., Chem. Commun.*, 1992, 784.

[‡] The σ - π interactions between porphyrin HOMO(A_{2u}) and bonding orbital of 3c-4e bond and between porphyrin LUMO(E_g) and antibonding orbital of 3c-4e bond are considered to have an essential importance. Through the σ - π interactions, the photoexcitation of porphyrin ring could enhance the dissociative character of the 3c-4e bond.