afford a cyclic cogged dimer with sixteen π-stacked tetrapyrrole units, further studies are aimed at developing molecules which are potential models for systems such as the array of tetrapyrroles in the light-harvesting component of the bacterial light harvesting complex LH2.[14] Indeed, we note that the B800 and B850 components of the light-harvesting complex II in *Rhorospirillum molischianum* consist of eight and sixteen units of bacteriochlorophyll, respectively.[15]

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[12] Crystallographic details for **8**: $C_{141.75}H_{128}N_{16}Ni_4O_{5.75}$, dark green, octahedral crystal (0.15 × 0.10 × 0.10 mm), tetragonal space group $P4_122$ (no. 92); $a = b = 23.510(3)$, $c = 100.61(2)$ Å, $V = 55609(16)$ Å^3, $Z = 16$. Of 33061 reflections measured, 15009 were unique and 9740 observed ($R_{int} = 0.033$, $T_{min} = 0.90$, $T_{max} = 0.85$, $\mu = 1.047$ mm^{-1}, $\rho_{calcd} = 1.138$ g cm^{-3}); $R1 = 0.1142$ (observed data, $I > 2\sigma(I)$) and $wR2 = 0.3483$ (all data) for 2571 parameters. Data were collected at 113(2) K on a Siemens Hi Star multiwire proportional counter diffractometer mounted on a Rigaku RU300 rotating anode equipped with a 3.0 × 0.3 mm focal cup and Göbel mirrors ($Cu_{K\alpha}$ irradiation; $\lambda = 1.54178$ Å, ω scan mode, $2\theta_{max} = 90.2°$). The structure was solved by direct methods and refined (based on F^2 with all independent data) by full-matrix least-squares methods (Siemens SHELXTL Version 5.03). A total of fourteen methanol sites were found; twelve were located in regions of void, and the other two in the calixarene cavities. All sites showed only partial occupancy summing to a total of 1.75 methanol molecules. With the exception of the solvent molecules, non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generated by idealized geometry and treated as riding using isotropic thermal parameters (but not on the solvent molecules). The data were corrected for absorption [13]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100523. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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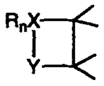
Synthesis, Structure, and Double Olefin Extrusion of All Three Diastereomers of 2,2,6,6-Tetrakis(4-chlorophenyl)-3,7-dimethyl-4-phenyl-1,5-dioxa-4λ^5-phosphaspiro[3.3]heptane**

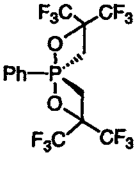
Takayuki Kawashima,* Rei Okazaki, and Renji Okazaki*

In the course of our study on heterocyclobutanes **1**[1] bearing highly coordinated main group elements at the position adjacent to the heteroatom we have reported the syntheses and isolation of intermediates of the Wittig and Peterson-type reactions.[2] Recently we also achieved the synthesis of tetracoordinate and pentacoordinate 1,2-oxathietanes and their thermolysis to the oxirane with retention of configuration.[3] Our studies on the influence of ring size on the stability of 1,2-oxaphosphetanes led to the synthesis of **2**, the first stable pentacoordinate spirophosphorane with two 1,2-oxaphosphetane rings; the stability is attributed to the trifluoromethyl groups at the 4-position.[4, 5]



1

X= P, Si$^-$, Ge$^-$, Sn$^-$,
S, Se
Y=O, NPh



2

Unexpectedly, however, double olefin extrusion from **2** was unsuccessful, because of the electronic effect of the strong electron-withdrawing groups. Taking into consideration the bonding character of equatorial bonds in a trigonal-bipyramid (TBP) structure, an electron-releasing group such as an alkyl group at the 3-position is expected to stabilize a TBP structure sufficiently even in the absence of a strong electron-withdrawing group. The introduction of such a substituent at the 3-position may also lead to kinetic stabilization toward hydrolysis by steric protection, as observed in the tetracoordinate 1,2-oxathietanes.[3a] We now report the synthesis, crystal structures, and thermolysis of all three diastereomers of 2,2,6,6-tetrakis(4-chlorophenyl)-3,7-dimethyl derivatives **3**.

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[*] Prof. Dr. T. Kawashima, Prof. Dr. Renji Okazaki, Rei Okazaki
Department of Chemistry, Graduate School of Science
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113 (Japan)
Fax: Int. code +(3)5800-6899
e-mail: takayuki@chem.s.u-tokyo.ac.jp

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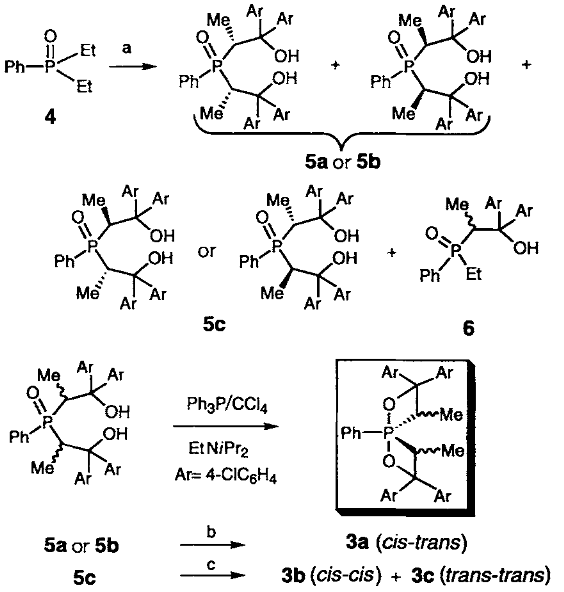
Sequential treatment of diethylphenylphosphane oxide (**4**) with *n*BuLi, 4,4'-dichlorobenzophenone, and aqueous NH_4Cl gave a diastereomeric mixture of bis(β-hydroxyalkyl)phosphane oxides (**5a–c**) along with a diastereomeric mixture of monohydroxyalkyl derivatives **6** (35%). Cyclization and dehydration of **5a** or **5b** by Appel's method[6] gave the *cis-trans* isomer **3a**, while similar treatment of **5c** provided a mixture of the *cis-cis* isomer **3b** and the *trans-trans* isomer **3c** (Scheme 1). The two oxaphosphetane rings of the *cis-trans* isomer **3a** are different from each other, while those of the *cis-cis* and *trans-trans* isomers **3b** and **3c**, respectively, were equivalent.



Scheme 1. a) 2.3 molar equiv *n*BuLi, THF, −78 → 25 °C, 10 min; 2.19 molar equiv 4,4'-dichlorobenzophenone, THF, −78 °C, 1 h; −78 → 25 °C; 25 °C, 2 h; aqueous NH_4Cl; b) **5a**: CH_3CN, 25 °C, 7 h; **5b**: CH_3CN, 40 °C, 8 h; c) CH_3CN, 25 °C, 6.5 h.

The X-ray crystallographic analysis of all three diastereomers showed that **3a** and **3b** have a distorted TBP structure with two oxygen atoms at apical positions, while **3c** has a distorted square-pyramidal (SP) structure with the phenyl carbon atom at apical and the other four atoms at basal positions, respectively (Figures 1 and 2).[7] In the crystal structure of the *cis-trans* isomer **3a** (TBP → SP[8] 19.0%) the apical bond angle deviates by 12.08(10)° from linearity. Deviations in the range between 10 and 20° are a common structural feature of hypervalent species containing a four-membered ring.[1a, b, 3b] On the other hand, in the *trans-trans* isomer **3c** (TBP → SP 73.7%) the apical P–C(Ph) bond length was 1.796(7) Å, while the basal P–C bond lengths were 1.835(7) and 1.829(7) Å, indicating that the apical bond is stronger than the basal bonds in an SP structure.

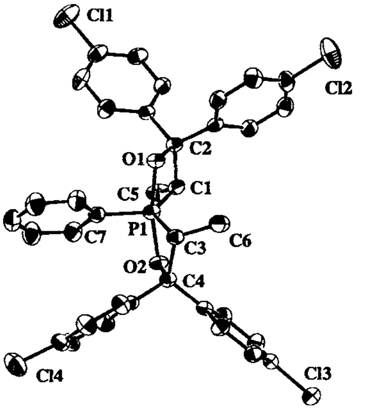


Figure 1. Structure of *cis-trans* **3a** (ORTEP drawing, thermal ellipsoid plots for 30% probability). Selected bond lengths [Å], bond angles [°], and torsion angles [°]: P1–O1 1.738(2), P1–O2 1.741(3), P1–C1 1.819(3), P1–C3 1.825(3), P1–C7 1.798(3); O1-P1-O2 167.92(10), C1-P1-C7 120.2(1), C1-P1-C3 128.0(1), C3-P1-C7 111.8(1), P1-C1-C2 89.4(2), C1-C2-O1 96.2(2), C2-O1-P1 96.4(1), O1-P1-C1 77.9(1), P1-C3-C4 87.9(2), C3-C4-O2 96.1(2), C4-O2-P1 95.1(2), O2-P1-C3 77.9(1), P1-C1-C2-O1 2.2(2), P1-C3-C4-O2 13.8(2).

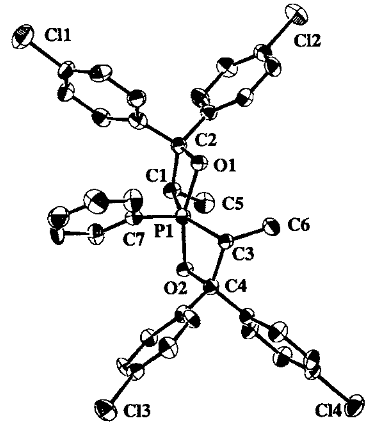


Figure 2. Structure of *trans-trans* **3c** (without Et_2O, ORTEP drawing with thermal ellipsoid plots for 30% probability). Selected bond lengths [Å], bond angles [°], and torsion angles [°]: P1–O1 1.719(4), P1–O2 1.715(4), P1–C1 1.835(7), P1–C3 1.829(7), P1–C7 1.796(7); O1-P1-O2 157.5(2), C1-P1-C7 108.8(4), C1-P1-C3 142.8(3), C3-P1-C7 108.4(4), P1-C1-C2 88.3(5), C1-C2-O1 95.6(5), C2-O1-P1 95.6(4), O1-P1-C1 76.7(3), P1-C3-C4 87.8(4), C3-C4-O2 95.6(5), C4-O2-P1 95.6(4), O2-P1-C3 77.4(3); P1-C1-C2-O1 15.2(4), P1-C3-C4-C2 14.6(4).

The ^{31}P NMR spectrum of **3c** in solution showed a peak at $\delta = -33.6$, which is similar to the values observed in the ^{31}P NMR spectra of **3a** ($\delta = -31.2$) and **3b** ($\delta = -32.7$), indicating that **3c** also has a TBP structure in solution.[9] Interestingly, the large difference in crystal structure between **3a,b** and **3c** is probably attributable to crystal packing forces, in other words, the energy difference between TBP and SP structures is quite small in this system as usual. Taking into consideration the high moisture sensitivity of a 3,7-unsubstituted derivative of **3**, it becomes clear that the electropositive substituents (CH_3) at the equatorial positions stabilize the TBP structure both thermodynamically and kinetically—evidently with support from the 4-chlorophenyl groups at the β-carbon atoms of the apical ligands.

Thermolysis of these compounds gave the corresponding olefin **7**, the ring-opened isomer of **3** (**8**), the dehydration product of **8** (**9**), and **5**. Interestingly, although the yields of the olefin are only moderate, they indicate that in sharp contrast to the thermolysis of **2**, one molecule of **3** afforded two molecules of the olefin by a double olefin extrusion (Table 1). Monitoring the reaction by NMR spectroscopy showed that there is an equilibrium between **3b** and **3c** during the reaction. Such an equilibrium has previously never been observed in pentacoordinate 1,2-oxaphosphetanes with two apical oxygen atoms.[10] Fur-

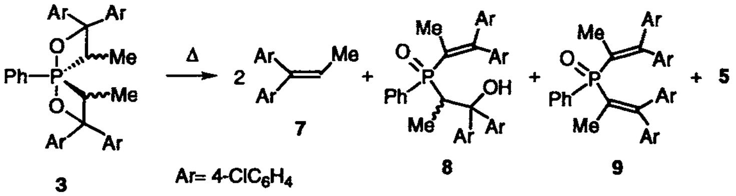


Table 1. Yields of products in the thermolysis of **3**. (Solvent C_6D_6, T = 80 °C.)

Entry	**3**	t	Additive	Yield [%][a]			
				7	**8** [b]	**9**	**5**
1	**3a**	6 h	–	55	49(16:33)	23	traces
2	**3b**	6 h	–	29	62(51:11)	16	7
3	**3b**	6.5 d	EtNiPr$_2$	158	–	4	–
4	**3b**	20 h	EtNiPr$_2$·HCl	127	27(>100:1)	9	–
5	**3c**	5 h	–	67	36(>100:1)	10	20

[a] Based on **3** and determined by ^{1}H NMR spectroscopy. [b] The ratio of two diastereomers is shown in parentheses.

thermore, the thermolysis of **3b** in the presence of Et(iPr)$_2$N and Et(iPr)$_2$N·HCl afforded the olefin in 158 and 127% yields, respectively (Table 1, entries 3 and 4). Judging from the longer reaction time of these reactions than that without an additive (entry 2), it is conceivable that the additives do not accelerate the olefin formation reaction, but retard the side reactions. Although we have no real evidence at present it is most likely that coordination of amine or chloride ion to the phosphorus center plays an important role in reducing the acidity of the methine proton. Further investigations on the effects of additives are in progress.

Experimental Section

nBuLi (1.64 M solution in hexane, 14.6 mL) was added to a solution of PhP(O)Et$_2$ (**4**) (1.89 g, 10.4 mmol) in dry THF (30 mL) at −78 °C under argon. The reaction mixture was stirred at room temperature for 10 min, and cooled again to −78 °C. A solution of 4,4'-dichlorobenzophenone (5.73 g, 22.8 mmol) in THF (30 mL) was added to the cooled solution at −78 °C. After stirring at −78 °C for 1 h, the reaction mixture was allowed to warm to 25 °C, stirred for 2 h, and then treated with aq NH$_4$Cl and extracted with CH$_2$Cl$_2$. The extracts were dried over anhydrous MgSO$_4$. After removal of the solvent under reduced pressure the residue was subjected to dry column chromatography to afford diastereomeric mixtures of **5** and **6** (1.25 g, 35%). These were purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$), flash column chromatography (SiO$_2$, CH$_2$Cl$_2$/hexane, 3/2), and recrystallization (CH$_2$Cl$_2$). Yields based on ^{1}H NMR data: **5a**, 6.9%; **5b**, 19%; **5c**, 25%.

5a: Colorless crystals; m.p. 225.0–226.0 °C (decomp); elemental analysis calcd for C$_{36}$H$_{31}$O$_3$Cl$_4$P (%): C 63.18, H 4.57, Cl 20.72; found: C 63.22, H 4.77, Cl 20.71; ^{1}H NMR (500 MHz, CDCl$_3$, 27 °C, TMS): δ = 1.44 (dd, ^3J(H,P) = 15.0 Hz, ^3J(H,H) = 7.3 Hz, 6H, CH$_3$), 3.42 (quint, ^3J(H,H) = ^2J(H,P) = 7.3 Hz, 2H, CH), 5.35 (s, 2H, OH), 6.76–6.79 (m, 4H, 4-ClC$_6$H$_4$), 6.96–7.04 (m, 6H, Ar), 7.09–7.14 (m, 2H, Ph), 7.17–7.20 (m, 4H, 4-ClC$_6$H$_4$), 7.26–7.29 (m, 4H, 4-ClC$_6$H$_4$), 7.33–7.38 (m, 1H, Ph); ^{31}P{^{1}H} NMR (109 MHz, CDCl$_3$, 27 °C, 85% H$_3$PO$_4$): δ = 56.7.

To a solution of phosphane oxide **5a** (59 mg, 0.087 mmol) and Ph$_3$P (228 mg, 0.87 mmol) in CH$_3$CN (6 mL), Et(iPr)$_2$N (0.15 mL, 0.86 mmol) and CCl$_4$ (0.084 mL, 0.87 mmol) were syringed at 25 °C. After the mixture had been stirred for 7 h, *cis-trans* **3a** precipitated out (24 mg). The precipitates were filtered and the filtrate was subjected to column chromatography (SiO$_2$, CH$_2$Cl$_2$: hexane = 1:1) to afford *cis-trans* **3a** (23 mg, total yield was 81%). A similar reaction (40 °C, 8 h) using **5b** instead of **5a** gave **3a** (42%), while the reaction (25 °C, 6.5 h) using **5c** afforded a mixture of *cis-cis* **3b** (39%) and *trans-trans* **3**) (26%). Recrystallization from CH$_2$Cl$_2$/hexane gave an analytically pure sample, and single crystals suitable for X-ray crystallographic analysis were grown in ether/hexane.

cis-trans **3a**: Colorless crystals; m.p. 119.5–120.5 °C (decomp); elemental analysis calcd for C$_{36}$H$_{29}$O$_2$PCl$_4$ (%): C 64.88, H 4.38, Cl 21.27; found: C 64.81, H 4.57, Cl 20.88; ^{1}H NMR (500 MHz, CDCl$_3$, 27 °C, TMS): δ = 0.94 (dd, ^3J(H,H) = 8.4 Hz, ^3J(H,P) = 26.3 Hz, 3H, CH$_3$), 1.35 (dd, ^3J(H,H) = 8.0 Hz, ^3J(H,P) = 27.4 Hz, 3H, CH$_3$), 4.24 (dq, ^2J(H,P) = 16.7, ^3J(H,H) = 8.4 Hz, 1H, CH), 4.58 (dq, ^2J(H,P) = 25.6, ^3J(H,H) = 8.0 Hz, 1H, CH), 6.96–7.09 (m, 9H, Ar), 7.20–7.35 (m, 10H, Ar), 7.87–7.96 (m, 2H, o-H of Ph); ^{31}P{^{1}H} NMR (109 MHz, CDCl$_3$, 27 °C, 85% H$_3$PO$_4$): δ = −31.2.

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[7] Crystal data for **3a**; C$_{36}$H$_{29}$O$_2$PCl$_4$, M_r = 666.41, crystal dimensions 0.75 × 0.50 × 0.50 mm, monoclinic, space group $C2/c$, a = 26.95(3), b = 16.32(1), c = 19.94(2) Å, β = 131.43(5)°, V = 6578(13) Å^3, Z = 8, ρ_{calcd} = 1.346 g cm^{-3}, μ = 4.39 cm^{-1}, $F(000)$ = 2832. The intensity data ($2\theta < 55°$) were collected at 296 K on a Rigaku AFC7R diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation (λ = 0.71609 Å) and the structure was solved by direct methods (SIR92). The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 4357 observed reflections [$I > 3.00\sigma(I)$] and 388 variable parameters with $R(R_w)$ = 0.046(0.026). Crystal data for **3b**: C$_{36}$H$_{29}$O$_2$PCl$_4$, M_r = 666.41, crystal dimensions 0.30 × 0.25 × 0.15 mm, monoclinic, space group $P2_1/c$, a = 8.966(2), b = 19.366(4), c = 19.152(5) Å, β = 96.70(2)°, V = 3302(1) Å^3, Z = 4, ρ_{calcd} = 1.340 g cm^{-3}, μ = 4.38 cm^{-1}, $F(000)$ = 1376. The intensity data ($2\theta < 55°$) were collected at 296 K on a Rigaku AFC5R diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation (λ = 0.71609 Å) and the structure was solved by direct methods (SHELXS86). The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1511 observed reflections [$I > 2.00\sigma(I)$] and 388 variable parameters with $R(R_w)$ = 0.075(0.034). Crystal data for **3c**: C$_{36}$H$_{29}$O$_2$PCl$_4$·C$_4$H$_{10}$O, M_r = 740.53, crystal dimensions 0.65 × 0.50 × 0.05 mm, monoclinic, space group $C2/c$, a = 36.852(9), b = 10.001(8), c = 21.495(4) Å, β = 105.89(2)°, V = 7619(6) Å^3, Z = 8, ρ_{calcd} = 1.291 g cm^{-3}, μ = 3.88 cm^{-1}, $F(000)$ = 3088. The intensity data ($2\theta > 55.1°$) were collected at 296 K on a Rigaku AFC7R diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation (λ = 0.71609 Å) and the structure was solved by direct methods (SHELXS86). The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2424 observed reflections [$I > 3.00\sigma(I)$] and 433 variable parameters with $R(R_w)$ = 0.057(0.034). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-100363. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223)336-033: e-mail: deposit@chemcrys.cam.ac.uk).

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[9] This is also supported by the following observation that although the ^1J(C,P) (P-Ph) and ^1J(C,P) (P-CH) values of **3c** were expected to be larger and smaller than those of **3a** or **3b**, respectively, judging from the bonding character of the square-pyramidal structure, the values observed were similar to those of **3a** and **3b**.

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