Synthesis and X-Ray Crystal Structural Analysis of a Fully Unsaturated Tetraphosphole Macrocycle

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The reaction of the 5,5′-bis(formyl)-2,2′-biphosphole **1** with the *o*-xylylidene bis-ylide **2** affords the 24-membered tetraphosphole macrocycle **3** in 60% yield; the X-ray crystal structure of **3** shows an all-*trans* disposition of the four lone pairs and a diameter of the central cavity of *ca.* 6 Å.

Pyrroles form the basis of a wide range of macrocycles, which include the porphyrins, porphycenes and expanded porphyrins.[1] Their phosphorus analogues are unknown. With a correct tailoring of the macrocycle, taking into account the larger size of the phosphole ring than its nitrogen counterpart,[2] this kind of rigid tetradentate crown should certainly have a rich coordination chemistry, particularly towards soft, catalytically active, heavy transition metal centres. With such a goal in mind, we describe here the synthesis and X-ray crystal structure analysis of the first α,α′-connected tetraphosphole macrocycle. Our starting point is the 5,5′-biscarboxaldehyde **1**.[3] Upon reaction with the bis-ylide **2** at low temperature, it affords the expected tetraphosphole macrocycle **3** in a surprisingly high yield (60%).†

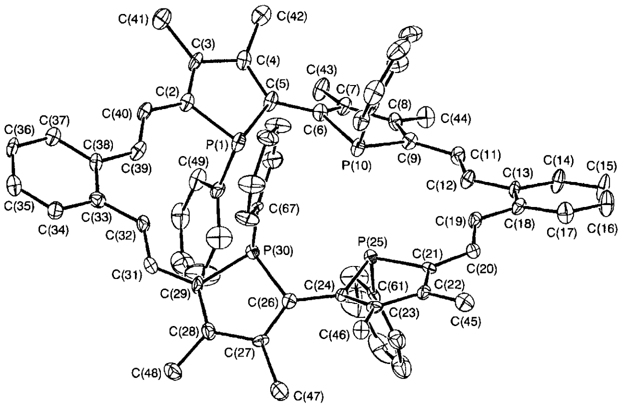
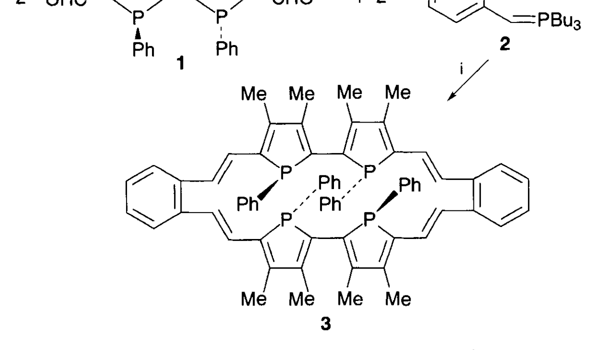


Fig. 1 Molecular structure of $C_{68}H_{60}P_4$ **3**, as determined by a single X-ray diffraction study. Selected bond lengths, distances (Å) and angles (°): P(1)–C(2) 1.807(5), P(1)–C(5) 1.822(5), P(1)–C(49) 1.830(6), C(2)–C(3) 1.356(7), C(2)–C(40) 1.438(7), C(3)–C(4) 1.469(6), C(4)–C(5) 1.364(6), C(5)–C(6) 1.450(6), C(33)–C(38) 1.428(7), C(38)–C(39) 1.473(7), C(39)–C(40) 1.336(7), $P_1 \cdots P_{10}$ 3.307, $P_1 \cdots P_{30}$ 5.202, $P_{10} \cdots P_{25}$ 5.060, $P_{25} \cdots P_{30}$ 3.302, $P_1 \cdots P_{25}$ 6.056, $P_{10} \cdots P_{30}$ 6.148, P(1)C(2)–C(5)/P(10)C(6)–C(9) 35.90 ± 0.24, P(25)C(21)–C(24)/P(30)C(26)–C(29) 38.66 ± 0.14, P(1)C(2)–C(5)/C(33)–C(38) 14.36 ± 0.52, P(10)C(6)–C(9)/C(13)–C(18) 16.81 ± 0.43, P(25)C(21)–C(24)/C(13)–C(18) 15.39 ± 0.43, P(30) C(26)–C(29)/C(33)–C(38) 28.46 ± 0.23.



Scheme 1 *Reagents and conditions*: i, THF, addition of **1** to **2** at −50 °C, then back to + 25 °C

The X-ray crystal structure analysis of **3**‡ shows a distorted 24-membered macrocycle with an all-*trans*-disposition of the four phosphorus-phenyl substituents which provide some steric protection to the central cavity. This hole is rather large as shown by the diagonal P···P distances *ca.* 6.1 Å. Otherwise, the four phosphole rings display quite normal bond distances and angles.

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Footnotes

† The bis-ylide **2** is obtained by reaction of the corresponding diphosphonium dibromide with *n*-butyllithium at −50 °C in THF until complete dissolution: δ ^{31}P **2** +7.4. See ref. 4 for synthesis of the Ph_3P analogue.

The crude macrocycle **3** is purified by chromatography on neutral alumina with hexane : diethyl ether 85 : 15 as the eluent. Deep-red crystals; ^{31}P NMR (CH_2Cl_2): δ +15.9; MS(EI): *m/z* 1000 (M^+, 100%), 500 (100%).

‡ *Crystal data* for **3**: Crystals of **3** $C_{68}H_{60}P_4 \cdot 1.5CH_2Cl_2$ were grown from a CH_2Cl_2–MeOH solution of the compound. Data were collected at −150 ± 0.5 °C on an Enraf-Nonius CAD4 diffractometer using Cu-Kα radiation (λ 1.54184 Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf-Nonius MOLEN package. The compound crystallises in space group $P\bar{1}$ (#2), a = 14.132(1), b = 16.884(2), c = 25.994(3) Å, α = 76.02(1), β = 79.03(1), γ = 85.36(1)°; V = 5904.58 (1.3) Å^3; Z = 4; D_c = 1.269 g cm^{-3}; μ = 27.8 cm^{-1}; $F(000)$ = 2364. A total of 10077 unique reflections were recorded in the range $3° \leqslant 2\theta \leqslant 100.0°$ of which 2862 were considered as unobserved [$F^2 < 3.0\sigma(F^2)$], leaving 7215 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms except one CH_2Cl_2 carbon atom. The latter could not be refined anisotropically as a result of a non resolvable disorder. Aside from minor conformational differences, the two independent molecules present in the asymmetric unit are identical. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were R = 0.048, R_w = 0.070, GOF = 1.54. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1, 1995.

References

1 For a short but recent overview of the field, see: J. L. Sessler, S. J. Weghorn, Y. Hiseada and V. Lynch, *Chem. Eur. J.*, 1995, **1**, 56.

2 For comparison : pyrrole : intracyclic < CNC *ca.* 109°, intracyclic N–C *ca.* 1.37 Å, N covalent radius 0.75 Å; phosphole : intracyclic < CPC *ca.* 90°, intracyclic P–C *ca.* 1.78 Å, P covalent radius 1.10 Å; see: P. Coggon and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, 1973, 1888.

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