Synthesis and *X*-Ray Structural Characterization of an Eight-membered P_4N_4 Cage Compound Analogue of S_4N_4 and α-P_4S_4

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The reaction of 1,3-di-t-butyl-2,4-dichlorodiazadiphosphetidine with Mg affords an unusual eight-membered cage compound $P_4(Bu^tN)_4$ whose structure has been determined by *X*-ray diffraction techniques.

There has been much recent interest in the systematic construction of rings and cages containing P–N bonds, and four-membered diazadiphosphetidine ring compounds should serve as useful precursors for larger rings and cages. For example, Scherer has reported the formation of $P_4(NCHMe_2)_6$ (**1**) which contains two superimposed diazadiphosphetidine rings coupled through the phosphorus atoms by bridging Pr^iN groups, and a thermolysis isomer, which has an adamantane-type structure.[1] In addition, Norman has reported the formation of a dinuclear diazadiphosphetidine $[(PhNH)P_2(NPh)_2]_2NPh$ (**2**) and a diazadiphosphetidine with a pendent $(PhNH)_2PNPh$ group (**3**).[2,3] We report here the formation of a novel cage compound $P_4(Bu^tN)_4$ (**4**), obtained from reduction of $\mathrm{Cl\overline{P(Bu^tN)P(Bu^tN)}Cl}$ (**5**) with Mg.

$$\underset{(\mathbf{1})}{\mathrm{P_4(NCHMe_2)_6}}$$

$$\underset{(\mathbf{2})}{\mathrm{[(PhNH)P_2(NPh)_2]_2NPh}}$$

$$\underset{(\mathbf{3})}{\mathrm{(PhNH)_2PN(Ph)\overline{P(PhN)P(PhN)}NHPh}}$$

$$4\,\underset{(\mathbf{5})}{\mathrm{Cl\overline{P(Bu^tN)P(Bu^tN)}Cl}} + 4\,\mathrm{Mg} \rightarrow \underset{(\mathbf{4})}{\mathrm{P_4(Bu^tN)_4}} + (\mathbf{4'}) + 4\,\mathrm{MgCl} \qquad (1)$$

A combination of (**5**)[4] (6 mmol) with excess of Mg chips in dry tetrahydrofuran was refluxed under nitrogen for 24 h, and the resulting slurry was filtered. The filtrate was evaporated to dryness, the residue was extracted with benzene, and (**4**) was recovered in approximately 60% yield as a slightly air sensitive colourless crystalline solid upon evaporation of the benzene [m.p. 148—152 °C, *m/z* 408 (M^+) ($C_{16}H_{36}N_4P_4$), ^1H n.m.r. (C_6D_6, ref. Me_4Si) δ 1.41 (s); ^{31}P {^1H} n.m.r. (ref. 85% H_3PO_4) δ 132.7 p.p.m. (s)]. A second, oily isomeric product (**4′**) was obtained from the benzene extract in about 40% yield. G.c. analysis of the reaction mixture shows two peaks with similar retention times, and the mass spectra of both fractions show the same parent ion. Full characterization of (**4′**) is in progress.

Crystal Data: $C_{16}H_{36}N_4P_4$ (**4**), $M = 408.45$, triclinic, space group $P\bar{1}$, $a = 10.490(3)$, $b = 10.550(3)$, $c = 12.168(3)$ Å, $\alpha =$

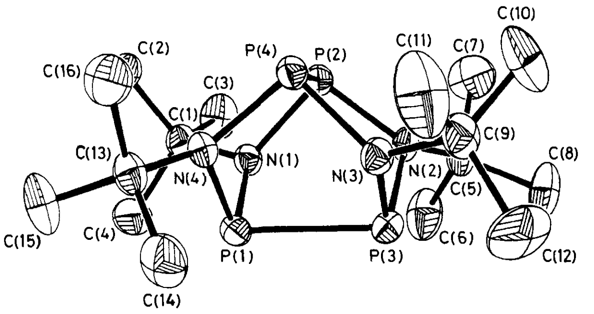

Figure 1. Thermal ellipsoid plot (30% probability ellipsoids) for $P_4(Bu^tN)_4$, showing the atom numbering scheme. Hydrogen atoms are omitted for clarity. Principal bond distances (e.s.d.s in parentheses) are: P(1)–N(1) 1.709(2), P(1)–N(4) 1.741(3), P(2)–N(1) 1.744(2), P(2)–N(2) 1.707(2), P(3)–N(2) 1.745(2), P(3)–N(3) 1.708(3), P(4)–N(3) 1.740(3), P(4)–N(4) 1.710(2), P(1)–P(3) 2.340(1), P(2)–P(4) 2.330(1) Å. Principal bond angles are: N–P–N(av.) 96.5(1)° and P–N–P(av.) 109.5(1)°.

99.68(2), $\beta = 105.92(2)$, $\gamma = 110.89(2)°$, $U = 1155.6(5)$ Å^3, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 3.3\ \text{cm}^{-1}$, $D_c = 1.17\ \text{g cm}^{-3}$. Intensity data were collected on a Syntex P3/F automated diffractometer operating in the ω scan mode and using Mo-K_α radiation ($\lambda = 0.71073$ Å, graphite monochromator). A total of 6741 unique reflections were measured at 20(2) °C with 4299 observed $[F \geqslant 5\sigma(F)]$. The structure was solved by direct methods (SHELXTL) and refined by block diagonalized least squares methods to give $R_F = 0.048$ and $R_{WF} = 0.050$.†

The reductive coupling of (**5**) is summarized in equation (1). Although the reaction appears simple, several P–N bond breaking and forming steps must accompany the coupling process. The structure of (**4**) has been unambiguously determined, and it is shown in Figure 1. The molecule has S_4 symmetry with the phosphorus and nitrogen atoms in bisphenoidal and square planar arrangements, respectively. This symmetry is consistent with the n.m.r. data, and the structure is related in a general way to the structures of S_4N_4[5] and α-P_4S_4.[6] The P–N bond lengths alternate with a long [av. 1.742(3) Å] and a short [av. 1.708(3) Å] distance associated with each phosphorus atom. The short P–N distance is similar to the diazadiphosphetidine ring P–N distances in (**1**) (1.70 Å) and slightly shorter than the related distances in (**2**) (1.723 Å) and (**3**) (1.72 Å). The long P–N bond distances in (**4**) are significantly longer than the average P–N bond distances in (**2**) and (**3**). The P–P distances in (**4**) [2.330(1) and 2.340(1) Å] are long compared to the normal range of P–P single bond distances (2.12—2.25 Å),[7] yet they are comparable to the related distances in α-P_4S_4 (2.353 Å)[6] and in P_4S_7 (2.35 Å).[8] The N–P–N and P–N–P angles (average values 96.5 and 109.5° respectively) differ significantly from the internal ring angles in (**1**)—(**3**) and (**5**)[9] [mean value: N–P–N 80(2) and P–N–P 100(1)°].

The $P_4(Bu^tN)_4$ cage reported here represents a missing member in a series of possible $P_x(NR)_y$ cage and ring compounds, and preliminary data suggest that (**4′**) is a skeletal geometric isomer of (**4**). Preliminary investigations of the reactions of (**4**) suggest that a number of interesting materials will be derived from this cage.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.