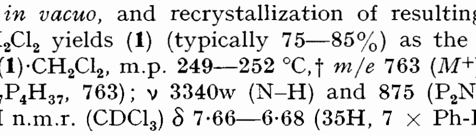
Synthesis and X-Ray Structure of a Dinuclear Cyclodiphosph(III)azane, $[(PhNH)P_2(NPh)_2]_2NPh$

By MARTIN L. THOMPSON, R. CURTIS HALTIWANGER, and ARLAN D. NORMAN*
(Department of Chemistry, University of Colorado, Boulder, Colorado 80309)

Summary The dinuclear cyclodiphosph(III)azane $[(PhNH)P_2(NPh)_2]_2NPh$ (**1**) is obtained in high yield from the reaction of aniline with PCl_3; a single crystal X-ray analysis shows that both cyclodiphosph(III)azane rings adopt a *cis* isomeric configuration.

CONSIDERABLE interest has been shown recently in cyclodiphosph(III)azanes because of their structural, bonding, and co-ordination properties.[1,2] We now report the first example of a novel dinuclear cyclodiphosph(III)azane, $[(PhNH)P_2(NPh)_2]_2NPh$ (**1**).



(1)

The slow addition of PCl_3 (0·20 mol) to a solution of $PhNH_2$ (0·95 mol) in toluene at 0 °C, followed by reflux for 2 h, filtration of $PhNH_3Cl$, evaporation of toluene from the solution *in vacuo*, and recrystallization of resulting solid from CH_2Cl_2 yields (**1**) (typically 75—85%) as the monosolvate, (**1**)$\cdot CH_2Cl_2$, m.p. 249—252 °C,† m/e 763 (M^+) (calc. for $C_{42}N_7P_4H_{37}$, 763); ν 3340w (N–H) and 875 (P_2N_2 ring) cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 7·66—6·68 (35H, 7 × Ph-H) and 3·51 [2H, 2 × NH, ^2J(P–H) 6·4 Hz]; ^{31}P n.m.r. (^1H decoupled, in toluene, AA′XX′ pattern) δ $-111{\cdot}8$ (P-1 and P-4) and $-107{\cdot}6$ (P-2 and P-3) p.p.m. [^2J(P-1–P-2) 6·4, ^2J(P-2–P-3) 3·0, and ^4J(P-1–P-3) 7·3 Hz, from spectral simulation].

Crystal data: $[(PhNH)P_2(NPh)_2]_2NPh\cdot CH_2Cl_2$, M = 763·703 (excluding CH_2Cl_2), monoclinic, a = 15·414(5), b = 18·668(8), c = 15·389(6) Å, β = 103·63(3)°, U = 4,303 Å^3, Z = 4, D_m = 1·32, D_c = 1·316 g cm^{-3}; μ(Mo-K_α) = 2·63 cm^{-1}, space group = $P2_1/c$. 2930 significant intensities ($2\theta_{max}$ = 50·0°) were recorded on a Syntex $P\bar{1}$ automated diffractometer, using graphite-monochromated Mo-K_α radiation. The data were corrected for Lorentz and

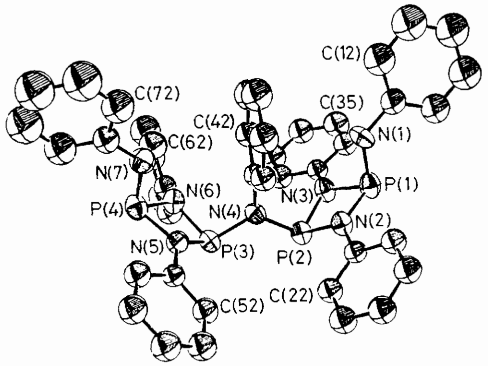


FIGURE. ORTEP drawing of $[PhNH)P_2(NPh)_2]_2NPh$ (**1**). Hydrogen atoms are omitted for clarity. Bond distances are: P(2)–N(4), **1·718**(7); P(3)–P(4), **1·702**(7); P(1)–N(1), **1·688**(8); P(4)–N(7), **1·687**(8); mean ring P–N, **1·723**(8); and mean P–C, **1·653**(9) Å. Bond angles are: mean ring N–P–N, **79·4**(3); mean ring P–N–P, **99·9**(3); P(2)–N(4)–P(3), **115·6**(4); and mean P–N–C, **126·3**(5)°.

---

† Satisfactory C, H, Cl, N, and P analyses were obtained for (**1**)$\cdot CH_2Cl_2$.

polarization factors but not for absorption. The structure was solved by direct methods using MULTAN and refined by full-matrix least-squares procedures. Phenyl rings were refined as groups with individual thermal parameters and all non-group atoms were refined anisotropically. After repeated refinement, a model with CH_2Cl_2 disordered with four overlapping, partially-occupied sites refined to a current R of 0·087 and R_W of 0·113.‡

The molecular geometry is shown in the Figure, which includes selected bonding parameters. The two cyclodiphosph(III)azane rings are joined by a bridging phenylimido group. All nitrogen atoms are essentially planar. The disposition of substituents on the phosphorus atoms of each ring is *cis*, suggesting interesting potential co-ordination properties for the compound. Mean ring P–N distances, and P–N–P and N–P–N angles are consistent with those reported recently for *cis*-$[(CH_2)_5NPN\text{–}Bu^t]_2$.[2]

Previous reports of the preparation of a mononuclear product $[(PhNH)PNPh]_2$ from $PCl_3\text{–}PhNH_2$ reactions now seem subject to question.[3] Studies of the mechanism of our reaction to determine how the dinuclear product forms and whether or not, under any conditions, mononuclear products might be obtained are in progress.

We thank the National Science Foundation for support.

(*Received*, 30*th March* 1979; *Com.* 332.)

---

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

[1] O. J. Scherer and G. Schnäbl, *Angew. Chem. Internat. Edn.*, 1976, **15**, 772; R. Keat and D. G. Thompson, *ibid.*, 1977, **16**, 797; M. Holstenberg and R. Appel, *Chem. Ber.*, 1978, **111**, 1815; R. Keat and D. G. Thompson, *J.C.S. Dalton*, 1978, 634; O. J. Scherer and G. Schnäbl, *Z. Naturforsch.* (*B*), 1976, **31B**, 1462; P. N. Hawker, L. S. Jenkins, and G. R. Willey, *J. Organometallic Chem.*, 1976, **118**, C44.

[2] R. Keat, A. N. Keith, A. MacPhee, K. W. Muir, and D. G. Thompson, *J.C.S. Chem. Comm.*, 1978, 372.

[3] Yu. G. Trishin, V. N. Chistokletov, V. V. Kosovtsev, and A. A. Petrov, *J. Org. Chem.* (*U.S.S.R.*), 1976, **11**, 1750 and references cited therein.