Synthesis and Structural Characterization of a New Class of Macrocycles Based on a Cyclodiphosphazane Skeleton†

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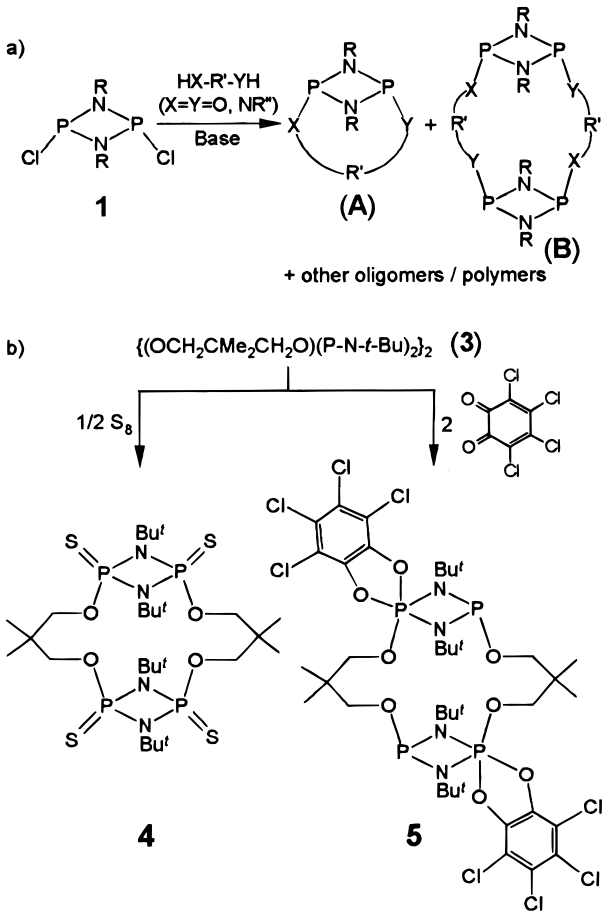
Received April 4, 2000

Cyclodiphosph(III)azanes $[ClPNR]_2$ (**1a**, R = *t*-Bu; **1b**, R = Ph) with two reactive ends (P−Cl bonds) can serve as valuable building blocks for developing new cages/macrocycles.[1,2] Elegant use of side groups like the aldehyde in $[(4\text{-}(CHO)C_6H_4O)PN\text{-}t\text{-}Bu]_2$ (**2**; obtained by starting with **1a**) can also lead to macrocycles containing a P_2N_2 skeleton.[3] An alternative approach is to treat **1** with a di- or polyfunctional reagent resulting in monomeric or oligomeric products (cf Scheme 1a). However, until now, the only products that have been structurally characterized in the reaction of **1** with difunctional reagents are the monomeric derivatives of type **A**.[1e,4−7] Herein we report the synthesis and structures of two novel macrocycles **4** and **5** obtained by the oxidation of **3** with sulfur and *o*-chloranil respectively (Scheme 1b);[8] compound **3** was prepared by reacting **1a** with 2,2-dimethyl-1,3-propanediol in the presence of Et_3N. The results clearly show that the precursor **3** has the composition $\{(OCH_2CMe_2CH_2O)(PN\text{-}t\text{-}Bu)_2\}_2$ which is the first example of a compound of type **B** (Scheme 1).[9]

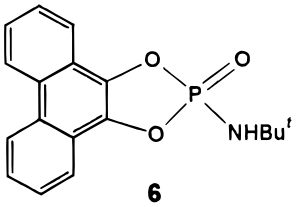
The X-ray structures of **4** (Figure 1) and **5**·$3C_6H_5CH_3$ (Figure 2)[10,11] reveal the *16-membered macrocycle* with two diol residues connecting the two cyclodiphosphazane units on each side. The P−N and P−O bond lengths are in the normal range in both compounds;[6,7,12−15] these distances are, however, shorter in **4** than in the tricoordinate compounds $\{2,6\text{-}Me_2C_6H_3O)PN\text{-}t\text{-}Bu\}_2$,[12] $\{[CH_2(4\text{-}Me\text{-}6\text{-}t\text{-}Bu\text{-}C_6H_2O)_2][PN\text{-}t\text{-}Bu]_2$,[7] or $\{(OCH_2CMe_2\text{-}CH_2O)(PNPh)_2\}$.[6] In compound **5**·$3C_6H_5CH_3$, the geometry around pentacoordinate phosphorus is severely distorted from a trigonal bipyramid [N(2)−P(1)−O(4) 165.92(14)°] although the greater length of the apical bonds [P(1)−N(2), P(1)−O(4)] is still retained. In solution this compound exhibits two doublets in the ^{31}P NMR at δ 82.8 and −39.0 for the tri- and pentacoordinate phosphorus atoms, respectively, which is consistent with its solid state structure.

Compound **5** is air-stable; its isolation is probably facilitated by the use of relatively more reactive *o*-chloranil (and hence lower reaction temperature) in this oxidative addition reaction. It is of interest to note that the addition products of cyclodiphosph(III)-azanes with diketones reported in previous studies were rather unstable.[6,16] Even in our case the only isolable product from the reaction of **3** with 9,10-phenanthrene quinone at 140−150 °C was

Scheme 1



6. {Mp: 240−242 °C dec. ^1H NMR ($CDCl_3$): δ 1.29 (s, 9H, *t*-Bu-*H*), 3.79 (d, 1H, N*H*), 7.63−8.73 (br m, 8H, Ar-*H*). ^{31}P NMR ($CDCl_3$): δ 21.2. MS: 327 [M^+].} We are yet to analyze the details of its formation.



To summarize, we have obtained novel macrocycles based on the cyclodiphosphazane skeleton. Isolation of these contrasts with

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† Dedicated to Prof. S. S. Krishnamurthy on the occasion of his 60th birthday.

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10.1021/ic000359o CCC: $19.00
Published on Web 09/14/2000

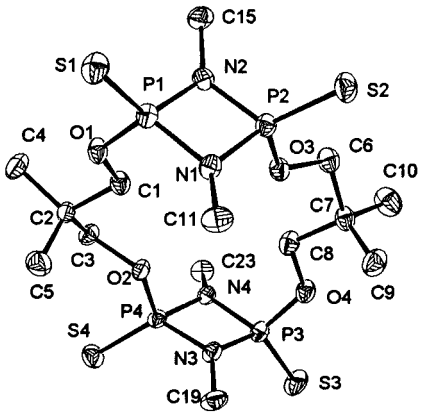

Figure 1. ORTEP drawing of **4**; only one of the two molecules in the asymmetric unit is shown. The other molecule has similar bond parameters. Terminal carbons on the N-*tert*-butyl group and hydrogen atoms are omitted for clarity. Selected bond parameter ranges: P−O 1.578(4)−1.584(4) Å, P−N 1.662(5)−1.684(4) Å, P−S 1.912(2)−1.923(2) Å, N−P−N 84.0(2)−84.7(2)°, P−N−P 94.9(2)−96.3(2)°.

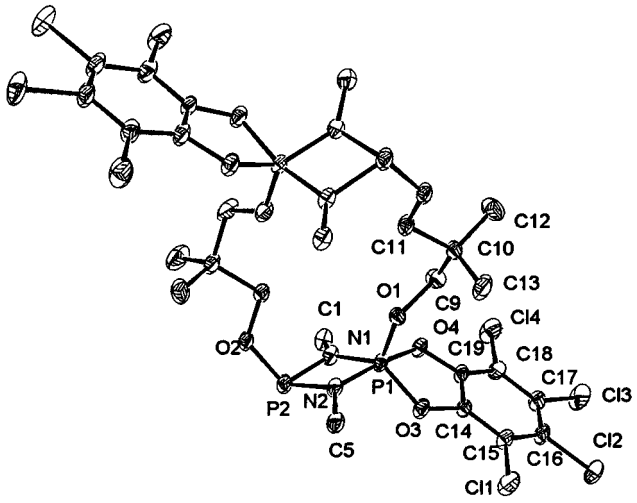

Figure 2. ORTEP drawing of $5\cdot3C_6H_5CH_3$; the solvent, terminal carbons on the N-*tert*-butyl group, and hydrogen atoms are omitted. Selected bond parameters: P(1)−N(1) 1.669(3) Å, P(1)−N(2) 1.706(3) Å, P(1)−O(1) 1.583(3) Å, P(1)−O(3) 1.676(2) Å, P(1)−O(4) 1.747(2) Å, P(2)−N(1) 1.723(3) Å, P(2)−N(2) 1.699(3) Å, P(2)−O(2) 1.612(2) Å, N(1)−P(1)−N(2) 81.74(14)°, O(1)−P(1)−N(1) 117.77(14)°, N(2)−P(1)−O(4) 165.92(14)°, N(1)−P(2)−N(2) 80.39(14)°.

that of monomeric (type **A**; Scheme 1) products [$(OCH_2CH_2CH_2O)(PNR)_2$] [**7a**, R = *t*-Bu;[17] **7b**, R = Ph[6]] obtained in the reaction of **1** with 1,3-propanediol. Thus these results leave sufficient scope to further explore the reactions of **1** with di- and polyfunctional reagents. It is also of interest to further investigate the chemistry of these macrocycles.

Acknowledgment. We acknowledge the Department of Science and Technology (New Delhi) for financial support and setting up a National Single Crystal Diffractometer Facility at the University of Hyderabad. K.C.K.S. thanks the AvH Foundation for donation of equipment.

Supporting Information Available: Two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Preparation of **4**: To compound **1a** (6.55 g, 23.8 mmol) in toluene (35 mL) was added dropwise a solution of 2,2-dimethyl-1,3-propanediol (2.48 g, 23.8 mmol) and Et_3N (4.85 g, 47.9 mmol) in toluene (25 mL), and the mixture was stirred at 25 °C for 12 h. Filtration followed by concentration of the solution to ca. 2 mL and addition of heptane (10 mL) resulted in the separation of **3** as a microcrystalline solid [3.01 g, 41%; δ(P) 139.2].[9] To 0.11 g (0.38 mmol) of **3** in toluene (10 mL) was added sulfur (0.05 g, 1.55 mmol), and the mixture was heated at 100 °C for 12 h. After concentration to 5 mL and addition of hexane (3 mL), compound **4** crystallized out along with unreacted sulfur (which could be separated by hand-picking). Yield: 0.12 g (84%). Mp: >290 °C. ^{1}H NMR ($CDCl_3$): δ 1.08 (s, 12 H, CH_3), 1.52 (s, 36 H, *t*-Bu-*H*), 3.80−3.90 (m, 8H, OCH_2). ^{31}P NMR ($CDCl_3$): δ 49.1. Anal. Calcd for $C_{26}H_{56}N_4O_4P_4S_4$: C, 42.12; H, 7.57; N, 7.56. Found: C, 42.05; H, 7.52; N, 7.34. Preparation of $5\cdot3C_6H_5CH_3$: To compound **3** (see above) (0.376 g, 0.61 mmol) in CH_2Cl_2 (5 mL) was added a solution of chloranil (0.301 g, 1.22 mmol) in CH_2Cl_2 (10 mL) dropwise over a period of 1 h at 25 °C. After stirring for 2 days, the solution was concentrated to 10 mL and toluene (3 mL) was added. Compound $5\cdot3C_6H_5CH_3$ crystallized after 2 days. Yield: 0.41 g, 78%. Mp: 264−266 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (s, 12 H, CH_3), 1.44 (s, 36 H, *t*-Bu-*H*), 3.62 (br, 8H, OCH_2). ^{31}P NMR ($CDCl_3$): δ 82.8 (d, P(III)), −39.0 (d, P(V)) [^2J(P−N−P) = 26.0 Hz]. Anal. Calcd for $C_{38}H_{56}Cl_8N_4O_8P_4$: C, 41.32; H, 5.08; N, 5.07. Found (after drying in a vacuum at 60 °C for 2 h): C, 41.46; H, 5.14; N, 4.95. Crystal data for **4**: $C_{52}H_{112}N_8O_8P_8S_8$, M = 1481.74, monoclinic, space group $P2_1$, a = 16.962(2) Å, b = 13.933(5) Å, c = 17.125(4) Å, β = 93.262(15)°, V = 4040.8 (19) Å^3, Z = 2, D(calc) = 1.218 Mg m^{-3}, μ = 0.427 mm^{-1}, total reflections 7659, independent reflections 7419 [R(int) = 0.0249]; data/restraints/parameters 7413/1/789, S (on F^2) 1.077, R1 [$I > 2\sigma(I)$] 0.0392, wR2 (all data) 0.0952, absolute structure parameter 0.07(8), largest diff. peak and hole 0.265/−0.236 e Å^{-3}. Crystal data for $5\cdot3C_6H_5CH_3$: $C_{59}H_{80}Cl_8N_4O_8P_4$, M = 1380.76, monoclinic, space group $C2/c$, a = 20.254(6) Å, b = 20.386(3) Å, c = 18.146(4) Å, β = 111.49(2)°, V = 6971(3) Å^3, Z = 4, D(calc) = 1.316 M gm^{-3}, μ = 0.467 mm^{-1}, total reflections 7033, independent reflections 6842 [R(int) = 0.0191]; data/restraints/parameters 6842/13/384, S (on F^2) 1.002, R1 [$I > 2\sigma(I)$] 0.0490, wR2 (all data) 0.1651, largest diff. peak and hole 0.352/−0.260 e Å^{-3}.
(9) On the basis of available data (elemental analyses and X-ray structures of five other compounds), **3** had been assigned a monomeric structure $(OCH_2CMe_2CH_2O)[PN$-*t*-$Bu]_2$.[7] The mass spectrum recorded later showed peaks at m/z 527, 439, and 307 [M + H]$^+$ in addition to a very low intensity peak at m/z 613 [2M + H]$^+$. We were not successful in obtaining suitable crystals for X-ray structure determination.
(10) X-ray data were collected on an Enraf-Nonius-MACH3 diffractometer at 293 K using Mo Kα (λ = 0.71073 Å) radiation and capillary mounting. Structures were solved and refined by standard methods.[11]
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