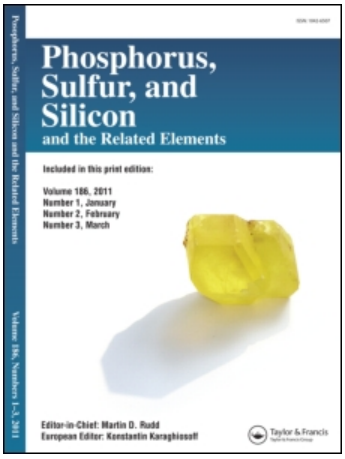

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TAKING A BITE OF PHOSPHORUS: UNUSUAL CLEAVAGE OF A PHOSPHORUS-CARBON BOND*

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The diphosphine $(Me_2N)_2PCH_2P(NMe_2)_2$ reacts with the tetraamino macrocycle cyclen at about 100 °C in a closed system via cleavage of the P-C bond to yield cyclenphosphorane and bis(dimethylamino)methylphosphine. The presence of dimethylamine in this reaction is necessary, since a similar reaction which allows the amine to escape, produces an oligomeric product of formula $[(C_8H_{16}N_4)PCH_2P]_n$.

Keywords: Phosphorus-Carbon Bond; Hypervalent; Dyphosphine; Cyclen

INTRODUCTION

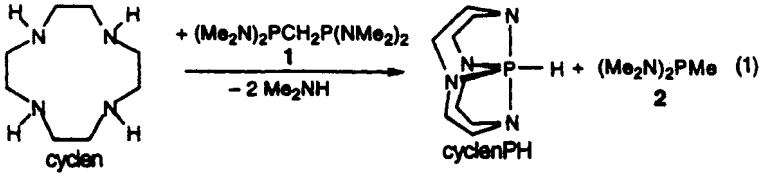
Our interests in the insertion of main-group elements into macrocycles has led to the isolation of novel "hypervalent" species of cyclen.[1] We have now begun a study on the insertion of more than one main-group element via the methylene-bridged diphosphine, $(Me_2N)_2PCH_2P(NMe_2)_2$, **1**.[2] Our expectations were that we would obtain species in which the PCH_2P unit bridged nitrogen atoms within a single cyclen macrocycle or between two macrocycles. However, our initial results with this reagent have led to a totally unexpected and remarkable P-C bond cleavage reaction which we herein report.

RESULTS AND DISCUSSION

When a mixture of **1** and cyclen is heated in toluene at temperatures between 85 – 110°C, the starting material disappears within 50 – 120 min. At this point,

* Dedicated to Professor Robert Wolf, a pioneer of organophosphorus chemistry in France.

the ^{31}P NMR spectrum shows two sharp resonances at δ 87 and -55. The upfield signal is totally unexpected and is in the pentacoordinate phosphorus range. Moreover, this signal exhibits a P-H coupling constant of 630 Hz, indicative of a direct P-H bond. This product was isolated and identified as cyclenPH by spectral comparison with a known sample obtained via the usual literature method.[3] Subsequent analysis of the other phosphorus-containing compound found it to be bis(dimethylamino)methylphosphine **2**, again by comparison with a separately obtained sample.[4]

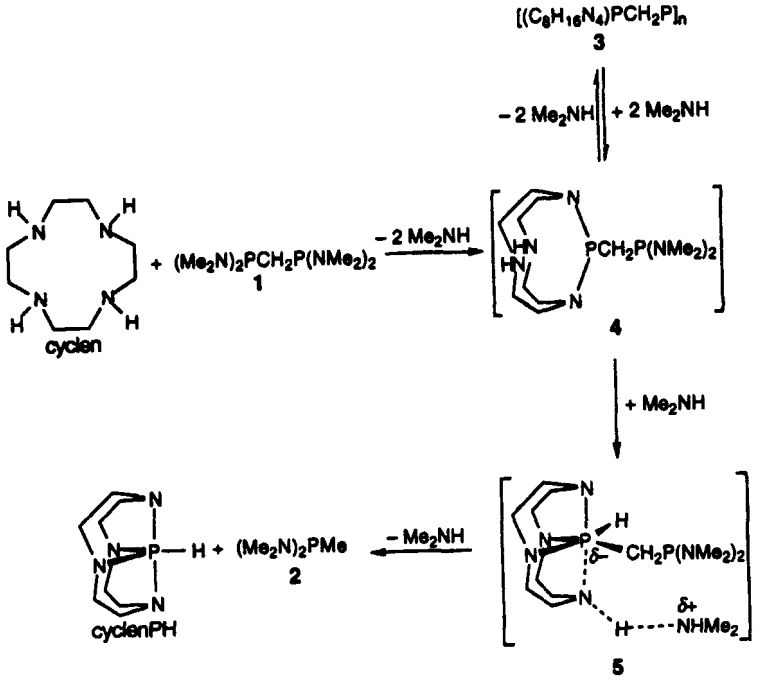


(1)

The presence of dimethylamine in this reaction is critical. The above results are obtained when the reaction is conducted in a closed system where the dimethylamine does not escape. If the reaction is conducted in an open system by refluxing in toluene, no cyclenPH or **2** is produced. Rather, another product **3** is formed which shows a broad signal in the ^{31}P NMR spectrum centered at δ107. This product is a mixture of oligomers in which the P-C-P unit is bound to cyclen via elimination of all four moles of dimethylamine. Elemental analyses and vapor pressure osmometry showed it to have the formulation $[(C_8H_{16}N_4)PCH_2P]_n$, where n has an average value of about 3.5. If this isolated sample is heated with dimethylamine in toluene at 100°C, the same P-C bond cleavage products are observed. Even in the closed system, this signal is present in the reaction mixture to a small extent along with the P-C bond cleavage products. However, if dimethylamine is added to the original reaction between cyclen and **1** in the closed system, the *only* products observed are cyclenPH and **2**.

From the above data, a pathway for the reaction can be postulated (Scheme 1). The initial product formed in the reaction between cyclen and **1** is a "monomer" which we tentatively assign the structure **4**. The binding of opposite nitrogens to the phosphorus, as shown, is based on the reported structure of a cyclen derivative in which sulfur binds in such a manner.[5] This can then convert to **3** via (a reversible) elimination of the remaining two moles of dimethylamine which readily occurs when the gaseous amine is allowed to escape. In the presence of dimethylamine the formation of **3** is inhibited, and the reaction proceeds via closure of the ring around phosphorus. We postulate this last transformation to occur through an intermediate **5** which involves initial N-H oxidative addition to phos-

phorus and formation of a six-coordinate geometry via nucleophilic attack of the remaining nitrogen. Although six-coordinate phosphorus is well-known, such a geometry would be too highly strained within the cyclen ring. To relieve this strain, the $CH_2P(NMe_2)_2$ anion leaves and is protonated to give the final products.



SCHEME 1

The conversion of **4** to final products is shown to also be assisted by the amine in Scheme 1. This was confirmed in a separate experiment in which a tertiary amine was added to the initial reaction. If our argument about the role of dimethylamine in the reversible conversion of **4** to **3** is correct, the addition of a tertiary amine should have no effect on that; however, if the role of base is important in the conversion of **4** to cleavage products, then an increase in the amounts of cyclenPH and **2** should be observed relative to **3**. In fact, this is exactly what occurs when trimethylamine is added to the reaction between cyclen and **1** (see Experimental).

It is important to note that the second phosphorus of **1** plays some role in this transformation, since we have tried the reaction of cyclen with **2** and observed no bond cleavage.

EXPERIMENTAL

All reactions and manipulations were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres Model DL-001-S-P dry box or using standard Schlenk techniques, unless otherwise indicated. Solvents were dried using standard procedures and distilled under a nitrogen atmosphere and either used immediately or stored in the dry box prior to use. Glassware was oven-dried at 140 °C overnight prior to use. The reagents cyclen[3b,6] and **1**[2] were prepared by standard literature methods. All NMR spectra were recorded on an IBM/Bruker WP200SY multinuclear NMR spectrometer (equipped with a Tecmag computer system) resonating at 200.132 (^{1}H) and 81.026 (^{31}P) MHz. ^{1}H resonances were measured relative to residual proton solvent peaks and referenced to Me_4Si. ^{31}P resonances were measured relative to external 85 % H_3PO_4. Elemental analyses were obtained from E + R Microanalytical Laboratories, Inc., Corona, NY, USA. Molecular weight VPO measurements were obtained from Galbraith Laboratories, Inc., Knoxville, TN, USA.

Isolation of 3. A mixture of **1** (0.154 g, 0.611 mmol) and cyclen (0.100 g, 0.580 mmol) in toluene (3 mL) was refluxed for 2 h . The volatiles were pumped off and the residue washed with hexane (3 x 5 mL) and pumped dry giving **3** as a colorless, crystalline product (70 %). Anal. Calcd for $C_9H_{18}N_4P_2$: C, 44.26; H, 7.43; N, 22.94. Found: C, 44.30; H, 7.42; N, 22.72. VPO: 832 ($CHCl_3$). ^{1}H NMR ($CDCl_3$): four broad overlapping peaks at δ 2.93, 3.13, 3.32, 3.52.

Sealed-tube reactions. A reaction tube equipped with a teflon stopcock was charged with **1** (0.154 g, 0.611 mmol), cyclen (0.100 g, 0.580 mmol), and toluene (2 mL). Then, gaseous dimethylamine (60 mL, 2.5 mmol) was condensed into the tube. The mixture was heated in an oil bath at 115°C for 55 min. NMR analysis of the reaction mixture showed only cyclenPH, **2,** the excess **1,** and dimethylamine. The volatiles were pumped off at 35°C and 0.01 torr. The remaining solid was sublimed at 100°C and 0.01 torr to yield pure cyclenPH (0.082 g, 71 %). In an analogous experiment with no added dimethylamine, the reaction mixture contained about 33 % of **3** relative to cleavage products. The addition of trimethylamine reduced this amount to about 18 %.

Acknowledgements

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