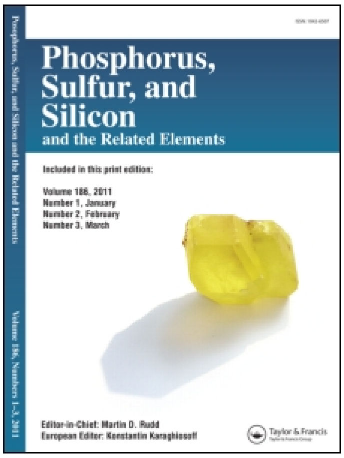


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# New Cavity-Containing Cyclophosph(III)azanes

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# NEW CAVITY-CONTAINING CYCLOPHOSPH(III)AZANES

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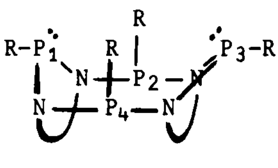
Abstract Reactions of 1,2-$(NH_2)_2C_6H_4$ with $RPCl_2$ (R = Me, Et) or $C_6H_4(NH)_2PMe$ with $MePCl_2$ and $Et_3N$ yield the novel cavity-containing rings $[C_6H_4N_2(\mu\text{-PR})(PR)]_2$. Mechanism of formation and the reactivity of these compared to the analogous $[C_6H_4N_2(\mu\text{-PPh})(PPh)]_2$ are described.

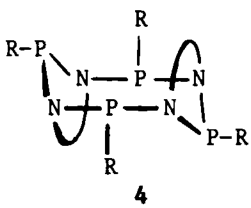


## INTRODUCTION

Molecules which contain donor atom functionality within a cavity or crevice are of considerable interest. Such molecules containing phosphorus(III) donor sites are rare. Recently we reported synthesis of a novel cavity molecule, $[C_6H_4N_2(\mu\text{-PR})(PR)]_2$ (**1**, R = Ph;  = 1,2-$C_6H_4$)[1] in



**1 - 3**

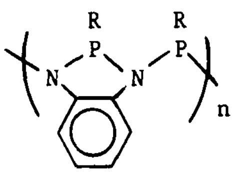


**4**

which the $P_4N_4$ ring is incorporated into a heteroatom bridged [3.3] orthocyclophane[2] structure. **1** contains endo P atoms ($P_1$ and $P_3$) separated by 3.2 Å whose electron pairs point between the vertically oriented phenyl groups ($Ph\text{-}P_1$, and $Ph\text{-}P_3$) creating the molecular cavity. Donor atoms $P_1$ and $P_3$ are expected to display highly selective reactivity. We now report further studies in which analogs of **1** are prepared, the cavity reactivity is explored, and the mechanism of ring formation is examined.

## DISCUSSION

Reactions of 1,2-$(NH_2)_2C_6H_4$ with $RPCl_2$ (R = Me, Et) in toluene in the presence of $Et_3N$ yield analogs of **1**, $[C_6H_4N_2(\mu\text{-PR})(PR)]_2$ (**2**, R = Me; **3**, R = Et). $^{31}P$ NMR spectra of reaction mixture exhibit resonances from **2** or **3** (2 t: **2**, δ 101.2 and 76.9, J = 19.2 Hz; 3, δ 110.5 and 83.2, J = 18.9 Hz) along with broad equal-area resonances (δ 80 - 110 and δ 52 - 80) from higher oligomers/polymers, **5**. **2** or **3** are not easily separated from 5; however, treatment of



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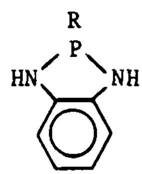


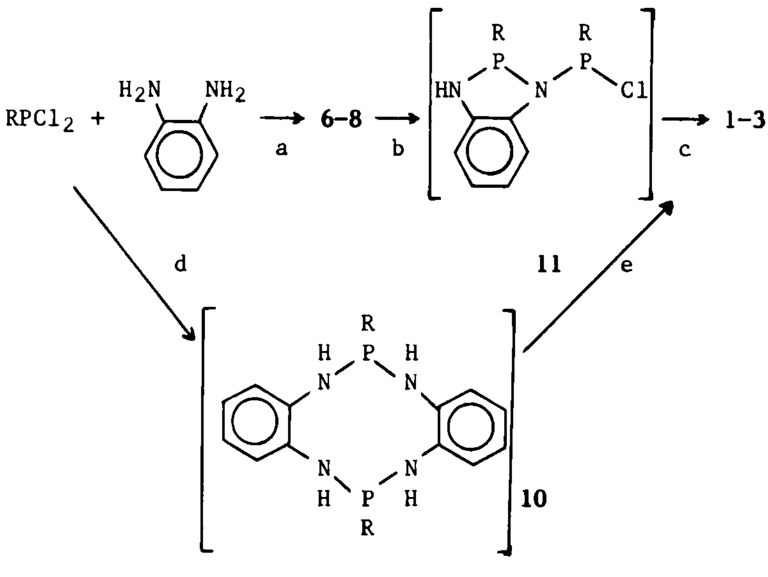
**6 - 9**

the reaction mixture with cycloheptatriene•$Mo(CO)_3$ insolubilizes the presumed polymer by $Mo(CO)_3$ coordination leaving **2** or **3** as major products. Although x-ray structures of **2** or **3** have not been obtained, comparisons of $^{31}P$ NMR spectral data with data for **1** indicate that **2** and 3, like 1, are cis isomers. No evidence for trans isomers (**4**) or higher cyclooligomers (**5**, n = 3, 4) is obtained. Tert-$BuPCl_2$/1,2-$(NH_2)C_6H_4$ reaction does not yield a product analogous to 1 - **3**, perhaps because of the large size of the t-Bu groups.

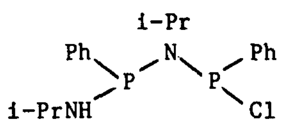
Phosphadiazoles useful in alternate syntheses of 1 - **3** and reaction mechanism studies have been prepared. $RP(NEt_2)_2$/1,2-$(NH_2)_2C_6H_4$ (1:1.2 m/m) reactions (R: Me, 4 hr, 55 °C; Et, 3 hr, 70 °C; Ph; 50 hr, 80 °C; t-Bu, 22 hr, 80 °C) yield $C_6H_4(NH)_2PR$ [R = Me (**6**), Et (**7**), Ph (**8**), t-Bu (**9**)] nearly quantitatively. Of particular interest, reactions of **6** with $MePCl_2$ and $Et_3N$ produce a mixture whose $^{31}P$ NMR spectra is virtually superimposable with those from 1,2-$(NH_2)_2C_6H_4$/$MePCl_2$ reactions above.

Higher cyclooligomers of **5** (e.g. n = 3, 4) are of interest; however, their existence as products in reactions which form **1** - **3** was not apparent. Consequently, alternate synthetic routes especially directed toward cyclotrimers $[C_6H_4N_2(\mu\text{-PR})(PR)]_3$ were examined. Two $Mo(CO)_3$ metal-templated reactions were studied. Reaction of the new complex fac-$[C_6H_4(NH)_2PMe]_3Mo(CO)_3$ [$^{31}P$ NMR ($CH_3CN$), δ 132.6] with $MePCl_2$ and $Et_3N$ yielded product tentatively characterized as $[C_6H_4N_2(\mu\text{-PMe})(PMe)]_3Mo(CO)_3$. Isomer composition remains to be established. Fac-$(MePCl_2)_3Mo(CO)_3$ when combined with three equivalents of $C_6H_4(NH)_2PMe$ and $Et_3N$ showed little reaction, possibly because of the high degree of steric crowding required for $(MePCl_2)_3Mo(CO)_3/C_6H_4(NH)_2PMe$ reaction.

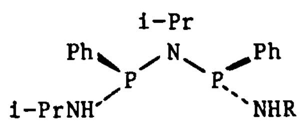
Details of the mechanism by which **1** - **3** form have been sought. Firstly, the point at which closure to diazole rings occurs is of interest since these rings are the apparent major source of structural rigidity and stability in the cavity molecules. Diazole rings could form early (a, below) and subsequently cyclocondense (b,c), or late (e) in reactions between $RPCl_2$ and an initially-formed (d) unstabilized $P_4N_4$ ring (**10**).



Based on the coincidence of product composition between the 6/-$MePCl_2$ and 1,2-$(NH_2)_2C_6H_4/RPCl_2$ reactions, early formation of the diazole ring (a) followed by diastereoselective cyclocondensation (b and c) appears likely. Secondly, stereochemical features of the reactions have been considered. Although direct observation of intermediates preceeding formation of **1** - **3** (e.g. **11**) has not yet been possible, information from related model systems proves useful. Studies of the i-$PrNH_2/PhPCl_2$ reaction show that diphosphinoamine **12** is the key intermediate preceeding diastereoselective formation of the product meso-$[PhP(i\text{-}PrNH)]_2Ni\text{-}Pr$ (**13**, R = i-Pr).




**12**




**13**

In general, **12** with $RNH_2$ (R = Et, t-Bu) yields selectively meso products **13**, R = Et, t-Bu). If similar stereo preference is exhibited in the formation of **11** and in subsequent reaction(s) of **11** to **1** - **3**, the cis-isomer specific formation of **1** - **3** can be rationalized.

Compounds **1** - **3** are unique when compared to $P_4N_4$ rings reported earlier. $(RNPR)_4$ (R = Me, Et)[4,5] and $[(n\text{-}Pr)\overline{NCH_2CH_2NP})]_4$[6] have 4-fold molecular symmetry and are "crown" shaped with only one type of P-atom environment. **1** - **3** are stable in solution; no evidence for cis-trans isomerism or dissociation to monomers or dimers[6] is seen. The rigidity of **1** - **3** make them cavity-containing molecules into which highly selective coordination of other atoms, small molecules, or metal moieties at the endo P atoms ($P_1$ and $P_3$) can be expected. The exo P atoms ($P_2$ and $P_4$) are cleanly oxidized by $S_8$ (2 hr, 84 °C), yielding $[C_6H_4N_2(\mu\text{-}PR)(RPS)]_2$ (R = Me, **14**; Et, **15**; Ph, **16**). Norbornadiene•$Mo(CO)_4$ does not react with **16** to form a $Mo(CO)_4$ complex. $S_8$ reacts only slowly with

**16** (7 days, 110 °C) to form a trisulfide. In contrast, **14** with $S_8$ (36 hr, 98 °C) forms a tetrasulfide product, indicating a significant difference in cavity reaction selectivity between **14** and **16**.

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