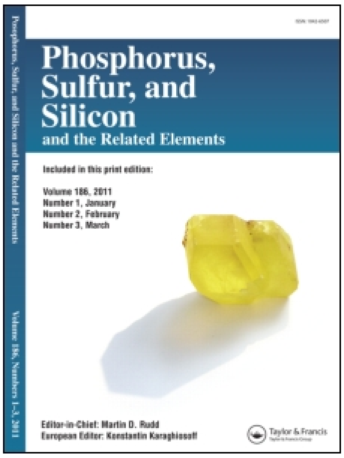

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DIASTEREOSELECTIVE FORMATION OF FUNCTIONAL DIPHOSPH(III)AZANES

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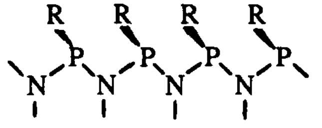
Abstract Diphosph(III)azanes i-PrN[PhP(i-PrNH)](PhPR) (R = Me, Et, Ph, t-Bu) form diastereoselectively in reactions of RNH_2 with i-PrN[PhP(i-PrNH)](PhPCl). Reactions of 1,3,2-diazaphospholes $C_6H_4(NH)_2PR$ with $RPCl_2$ and $RP(NEt_2)_2$ (R = Me, Ph) yield i-PrN[PhP(i-PrNH)][PhP(RNH)] and C_6H_4(NH)PRNP(R)X (X = Cl, NEt_2), respectively, with modest stereoselection. New diazaphosph(III)azanes are characterized by spectral (^{31}P, ^{1}H, ^{13}C NMR, IR, MS) data and single crystal x-ray analyses of i-PrN[PhP(i-PrNH)][PhP(EtNH)] and C_6H_4(NH)PEtS(N)P(NEt_2)EtS are described.

INTRODUCTION

The synthesis of oligomeric/polymeric phosph(III)azanes[1,2] and the subsequent investigation of their properties raises questions about how such systems might be obtained in stereoregular isotactic (1)[3,4] or syndiotactic (2) forms:



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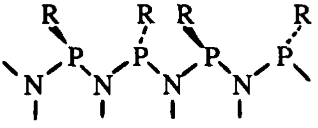

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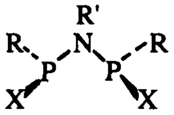
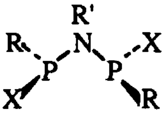
These could have significantly different properties from each other and from randomly formed atactic compounds. To date, stereoregular inorganic condensation polymers are largely undocumented.

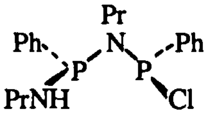
To develop routes to stereoregular polyphosph(III)azanes it is necessary to examine reactions by which >P-N(-)-P< bond units form. Since unsymmetrically substituted bis(phosphino)amines (3) are the minimal sized units needed to define a stereoregular linear phosphazane, reactions by which they arise become important.



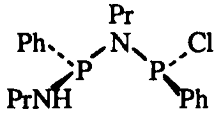
3A



3B



4A

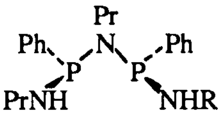


4B

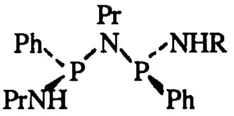
Although phosphorus(III) bis(phosphino)amines are known,[5] only a few containing chiral phosphorus atoms have been described. Our report of the formation of *meso*-i-PrN[PhP(i-PrNH)$]_2$ (**3A**; R = Ph, X = i-PrNH)[6] provided the first unambiguous evidence for diastereoselective bis(phosphino)amine formation. We now wish to report further related studies and recent attempts to prepare diastereoselected functional diphosphazanes which can be used in higher oligomer/polymer phosphazane synthesis.

DISCUSSION

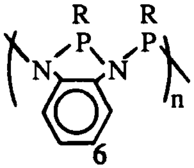
Reactions of the chloro(amino) bis(phosphino)amine **4** (Pr = i-Pr), which is formed as a 50:50 erythro (d,l)' [**4A**]: threo (d,l) [**4B**] mixture of diastereomers,[5] with primary amines (R = Me, Et, i-Pr, t-Bu, Ph) yield the bis(phosphino)amines **5A** and **5B** in ratios of 12:1



5A



5B



6

(R = Me), 24:1 (R = Et), 35:1 (R = i-Pr), 50:1 (R = Ph) and >50:1 (R = t-Bu). In each case, the compounds have been characterized by spectral (^{31}P and ^{1}H NMR, MS, and IR) data. That **5A**, the (d,l)' isomer is the major diastereomer from each reaction is confirmed by an x-ray single crystal analysis of the Et (Figure 1) and t-Bu derivatives.

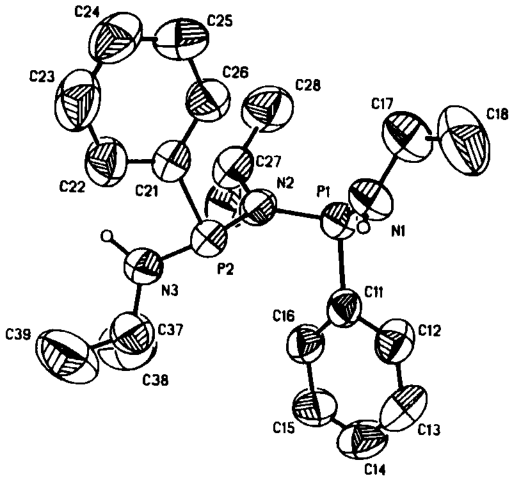
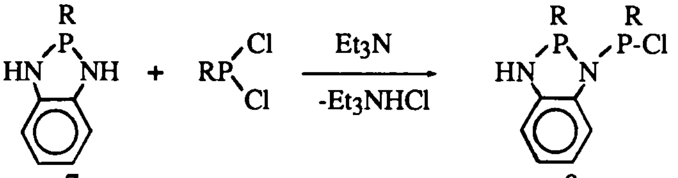


FIGURE 1. Structure of i-PrN[PhP(i-PrNH)][PhP(EtNH)] (**5A**, R = Et).

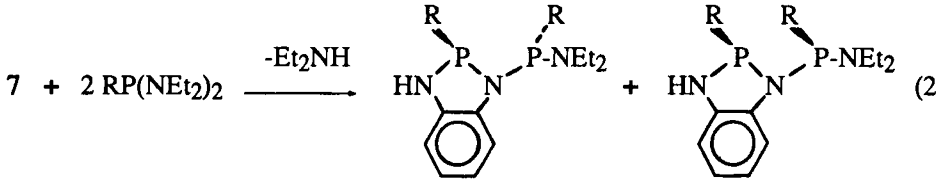
Reactions have been examined whereby chloro(amino) bis(phosphine) bond units might be obtained in skeletally stabilized molecules which could subsequently be used in higher phosphazane oligomer/polymer (**6**) synthesis. When $RPCl_2$ (R = Me, t-Bu, and Ph) reacts with the diazaphospholes (**7**) (R = Me, Ph) (reactant ratio 1:1) in the presence of Et_3N (to scavenge HCl) at temperatures below 0 °C,



7 **8** (1)

product mixtures are obtained which contain the previously reported $[C_6H_4N_2(PR)_2]_n$ oligomers/polymers (**6**)[1] in addition to minor amounts of product tentatively characterized as **8**. Two pairs of coupled, doublet $^{31}P\{^1H\}$ NMR resonances are observed in a a 4-6:1 ratio attributable to diastereomers of **8**. Attempts are being made to isolate and structurally characterize these diastereomers and to determine if the stereocontrol exhibited in the reaction (eqn. 1) parallels that observed in the conversion of **4** to **5A** and **5B**. If so, A-B type monomers[3] for syntheses of oligomers/polymers **6** might be available.

Transamination reactions also have been examined as routes to stereoselected functional bis(phosphino)amines. **7** with $RP(NEt_2)_2$ at 40 - 80 °C results in elimination of



9A **9B**

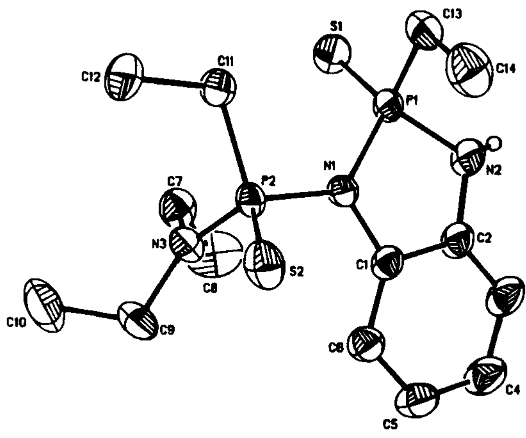


FIGURE 2. Structure of $[C_6H_4(NH)PEtS(N)P(NEt_2)EtS]$ (**10A**).

Et_2NH and formation of isomers of **9** (R = Et). Based on ^{31}P NMR spectral analysis, **9A** and **9B** are typically formed in a 2-3:1 ratio. The higher ratios are achieved at the lower reaction temperatures. **9A** and **9B** were converted to their corresponding phosphine sulfides **10A** and **10B** [$C_6H_4(NH)PEtS(N)P(NEt_2)EtS$] by reactions with elemental sulfur, and separated by flash chromatography. Subsequently, **10A** was crystallized. From an x-ray anaylsis it has been shown that **10A**, and indirectly **9A**, is the threo (d,l) diastereomer (Figure 2). It is of interest to note that the condensation reactions in eqns. 1 and 2 preferentially produce different diastereomers, forming the (d,l)' and (d,l) isomers, respectively.

Diphosphazanes **9A** and **9B**, and **8** if it can be obtained from its reaction mixture, constitute first examples of A-B type monomers that might be useful not only for extended phosphazane synthesis but also for stereoregular polymer formation. Such studies are in progress.

ACKNOWLEDGEMENT

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