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Facile Interconversion of Polyphosphides and Formation of a New Polyphosphide Anion

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The tendency to form element-element bonds is a characteristic that has been exploited in the inorganic chemistry of group 16 elements to yield a rich class of compounds including several polyatomic cationic and anionic species.[1] In the last 2 decades a challenge to this special feature of the chalcogens has appeared through the synthesis and characterization of a variety of polynuclear phosphorus compounds which exhibit a wealth of phosphorus−phosphorus bonded skeletal arrangements.[2−5] Through careful preparative techniques, these once exotic species have been isolated as both polyhedral anionic species and as organopolyphosphanes. The application of two-dimensional NMR spectroscopy has allowed their characterization and eliminated reliance on single-crystal X-ray diffraction. A key feature of these compounds is the prevalence of anionic heptaphosphorus (P_7) units as structural subunits of the higher polyphosphides.

The perceived instability of polyphosphorus anions as well as the methods employed in their synthesis have discouraged much exploration of their reactivity or of the features that control the selectivity of the products. In order to overcome these problems we undertook an exploration of the synthetic routes and the reactivity of polyphosphide anionic species. Our goals were to expand their accessibility and to define the features which influence the relative stability of these species in order to carry out "aimed isomerizations". To these ends, we report the surprising stability of the hexadecaphosphide dianion (P_{16}^{2-}), its facile interconversion with the henicosaphosphide trianion (P_{21}^{3-}), and the transformation of P_{21}^{3-} to a new tetradecaphosphide dianion, P_{14}^{2-}. Our approach relies on the reduction of soluble white phosphorus (P_4) with molten potassium.

A variety of methods have been used for the preparation of these homopolyatomic anions. One particularly efficient route is offered by the cleavage of P_4 with $LiPH_2$ which lead to the preparation of $Li_3P_7{\cdot}3(C_4H_{10}O_2)$ and $Li_2P_{16}{\cdot}8THF$.[6] Reaction of P_4 with Na gave mixtures of P_{16}^{2-} and P_{21}^{3-} in combination with other polyphosphides.[6,7] Oxidation of Li_3P_7 was reported to produce a mixture of anionic species with Li_3P_{21} as the main product.[8] Examples of single-crystal X-ray structural determinations for these species are reported for $[(C_6H_5)_4P]_2P_{16}$ and $[Li(12\text{-crown-}4)_2]_3P_{21}$ which were prepared in unreported yields.[9,10] These studies confirmed the proposals based on ^{31}P NMR spectroscopy.

A major problem associated with these synthetic methods has been their lack of selectivity; mixtures of anions and low yields are often the result of these procedures. In addition, the connection between the stoichiometry of the reaction and that of the products has not always been clear. Interestingly, there is one report that upon removal of the THF from $Na_3P_{21}{\cdot}15THF$ a mixture of P_{21}^{3-} and P_{16}^{2-} along with other polyphosphides was formed.[8]

Reaction of P_4 and K in an 8:1 stoichiometric ratio in refluxing THF/DME for 3 h yields a dark red-orange solution. Evaporation of the solvent and extraction with degassed ethanol gave a dark red solution of P_{16}^{2-} (**1**) as identified by ^{31}P NMR spectroscopy.[6] Solutions of this anion were thermally stable but decomposed rapidly when exposed to the atmosphere. The stability of P_{16}^{2-} in wet ethanol and sensitivity to oxidation contrasts with previous reports indicating sensitivity to hydrolysis but not to oxidation.[8]

In an effort to isolate this species, the ethanol was removed under vacuum to yield a dark red solid with a P/K ratio of 8:1 as determined by X-ray fluorescence (XRF).[11] This red solid was almost completely soluble in THF, but examination of the ^{31}P NMR spectrum of this deep orange solution showed that, rather than P_{16}^{2-} being observed, this solution possessed an NMR spectrum characteristic of P_{21}^{3-} (**2**).[8] A small amount of insoluble material was separated from this solution and confirmed to contain only phosphorus by XRF. Surprisingly, if the THF is removed from the mixture of P_{21}^{3-} and insoluble phosphorus and is replaced by ethanol, the ^{31}P NMR spectrum of P_{16}^{2-} is restored. These results are summarized in Figure 1 and establish clearly for the first time the redox interconversion of two homopolyatomic phosphorus anions.

The solvent control of this interconversion was further demonstrated by the observation that addition of THF to ethanol solutions of P_{16}^{2-} resulted in formation of mixtures of this anion and P_{21}^{3-}. Similar mixtures were noted when ethanol was added to THF solutions of P_{21}^{3-}.

These observations indicate the subtle influence of the solvent on the ability to coordinate and stabilize the potassium cation to reduction from the phosphorus anion. It appears the THF is able to stabilize this system with a more highly reduced phosphorus anion (average charge of -0.143/P) while ethanol favors the formation of a less reduced species (average charge of -0.125/P). This idea is similar to the stabilizing features observed for the alkali metal salts of the Zintl anions of groups 14 and 15 in which delocalization of the electrons from the polyanions back to the cation is prevented by alkali-metal cation complexation.[12]

The ability to produce pure polyphosphides in high yield allows the exploration of their reactivity in more detail. Alkylation and silylation of the P_{16}^{2-} and P_{21}^{3-} anions by reaction with alkyl and silyl halides has been demonstrated.[13] Attempts to introduce stannyl substituents by reaction of 3 equiv of Bu_3SnCl with THF solutions of P_{21}^{3-} gave a slow conversion of the dark orange solution to a light orange solution with

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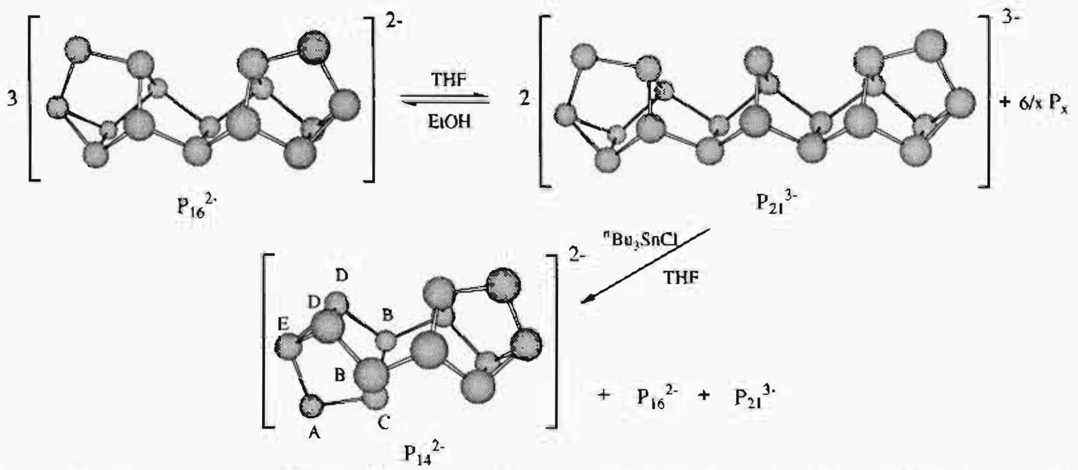

Figure 1. Summary of the interconversion of P_{16}^{2-} and P_{21}^{3-} and the formation of P_{14}^{2-}. The lettering scheme for P_{14}^{2-} corresponds to assignments of ^{31}P NMR resonances in Figure 2.

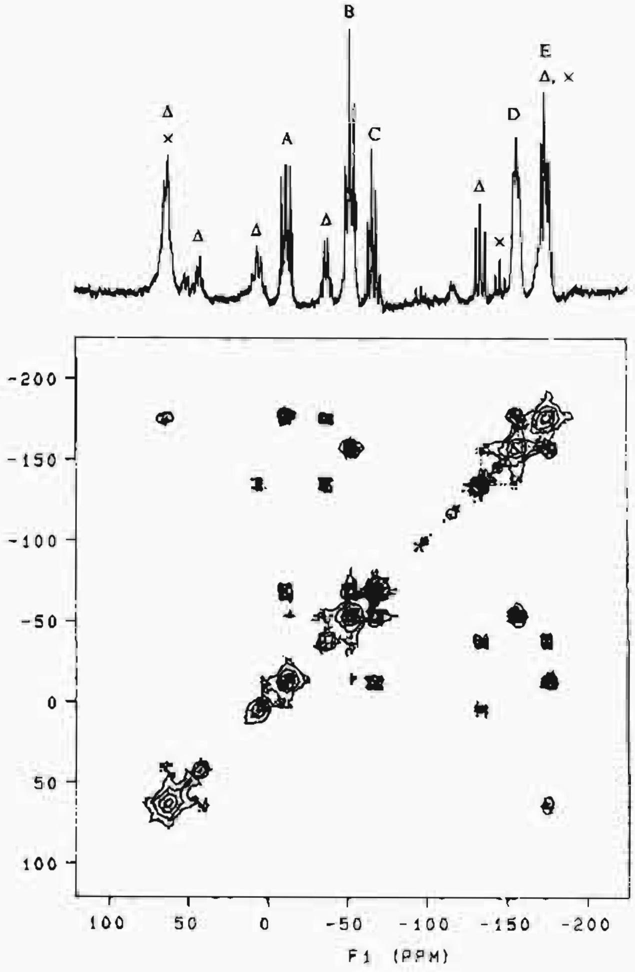

Figure 2. COSY-^{31}P NMR of P_{14}^{2-} in THF (256 × 256 matrix). Resonances indicated by letters are assigned to P_{14}^{2-} as indicated in Figure 1. Signals for P_{16}^{2-} and P_{21}^{3-} are indicated with Δ and ×, respectively.

formation of a precipitate. Separation of the solid and evaporation of the solvent yielded a light brown solid which was soluble in THF. This solid contained no tin when examined by XRF spectroscopy. A yellow solid was isolated from the THF solution by precipitation with hexane. The ^{31}P NMR spectrum of a THF solution of this solid exhibited four new signals at $\delta = -12, -53, -68, -156$, and -172 ppm with an intensity ratio of 1:2:1:2:1 along with small amounts of the characteristic ^{31}P NMR signals for P_{16}^{2-} and P_{21}^{3-}. The number, chemical shifts and integration of these signals do not correspond to any reported polyphosphides and are consistent with a new anion of formula $(P_7)_n^{n-}$ which is formed from *n* heptaphosphide anion subunits. Soluble anions of this general formula have not been isolated but have been proposed.[4,14] Solid state compounds with polymerized P_7^- units (MP_7, M = alkali metal) have been prepared. The structure of CsP_7[4] exhibits a linear polymer of P_7 units while those of LiP_7 and NaP_7[15] exhibit helical chain polymers due to opening of the three-membered rings. Apparently "KP_7" cannot be prepared with these structures.[4]

The lack of signals in the low field region of the NMR for this new material precludes the presence of the P_2 bridging units found in P_{16}^{2-} and P_{21}^{3-} while the high field signals for D and E indicate the likelihood that the three-membered rings, common to the P_7 subunits of the higher polyphosphides, are present in the new species. A substantial shift in the resonance for B to higher field would be expected for a smaller endocyclic bond angle that would result from the direct coupling of P_7 subunits.

Confirmation of the proposed structure is given by the homoscalar-correlated 2D-^{31}P NMR (COSY) spectrum (Figure 2). In this figure, all of the inequivalent and directly linked phosphorus atoms appear as cross peaks thus giving the connectivity of the new species. Due to the uniqueness of the proposed species and the presence of P_{16}^{2-} and P_{21}^{3-} in the reaction mixture, the interpretation of the ^{31}P NMR spectrum cannot be conclusive, and efforts to confirm the structure of this species by single crystal X-ray diffraction are underway. On the basis of the observed spectral features, the most direct suggestion is a P_{14}^{2-} species.

The surprising stability and facile interconversion of two polyphosphide anions has been demonstrated. A new phosphide anion, P_{14}^{2-}, has been prepared. We are continuing our efforts in defining the features which effect the stability of these species, the selectivity for a particular compound, and the reactivity of these polynuclear anions with organic and inorganic halides.

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Supplementary Material Available: Text giving experimental procedures for the described reactions. (1 page). Ordering information is given on any current masthead page.

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