

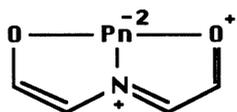
Chemistry of tricoordinate hypervalent pnictogens

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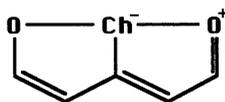
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Abstract - The chemistry of the first stable tricoordinate, hypervalent pnictogens (main group V elements) has been studied in a variety of diverse reactions. The observed reactivity patterns are in accord with detailed theoretical calculations. X-ray structural information has been obtained on a large number of systems. The information gained from these unusual systems has been used to propose and experimentally demonstrate a new *edge* inversion mechanism for tetrahedral main group element centers.

The 5-aza-2,8-dioxa-1-pnictabicyclo[3.3.0]octa-2,4,6-triene (ADPnO) (ref. 1) systems are the first examples of a 10-E-3 (ref. 2) bonding arrangement among the pnictogens (Main Group V elements N, P, As, Sb, Bi). Well known chalcogen 10-Ch-3 (Ch = S, Se, Te) systems (dioxachalcapentalenes, **1**) (ref. 3) are close structural and electronic analogues of the 10-Pn-3 ADPnO molecules but show somewhat different trends in electronics, structure and chemistry. The ADPnO systems are thus uniquely useful in understanding the factors which govern structure and chemistry at main group element centers.

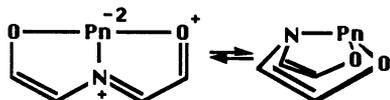


10-Pn-3 ADPnO
 Pn = P, As, Sb

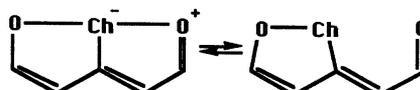


10-Ch-3 Dioxachalcapentalene (1)
 Ch = S, Se, Te

Many of the structural and electronic aspects of dioxachalcapentalene chemistry are influenced by the tendency for lateral distortions in these systems. The chemistry of ADPnO systems is subject to the influence of another type of geometric deformation not possible in the chalcogen series. Folding about the nitrogen to heavier pnictogen bond is possible in the ADPnO systems and is commonly manifested in the chemistry of the phosphorus derived system. This folding deformation maintains the connectivity between the tridentate ligand and the pnictogen center but results in different electronic properties at the pnictogen center. Conceptually, the folding deformation of the parent ADPnO molecules could lead to two near "ground state" geometric and electronic arrangements for the ADPnO systems (10-Pn-3 and 8-Pn-3). We have called the special type of isomerization associated with such 10-Pn-3 and 8-Pn-3 structures *electromorphism*.

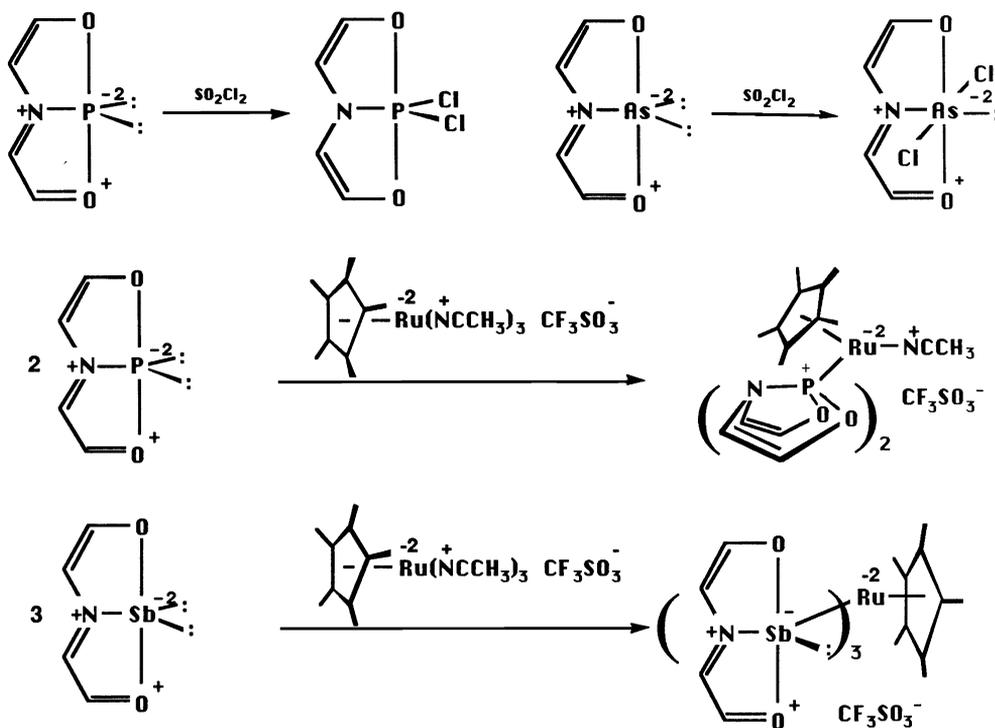


10-Pn-3 **8-Pn-3**
 Potential Electromorphism Possible in ADPnO Systems

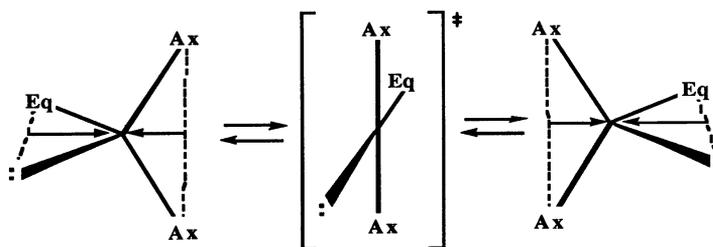


10-Ch-3 **8-Ch-2**
 Lateral Distortions Possible in Chalcogen Series

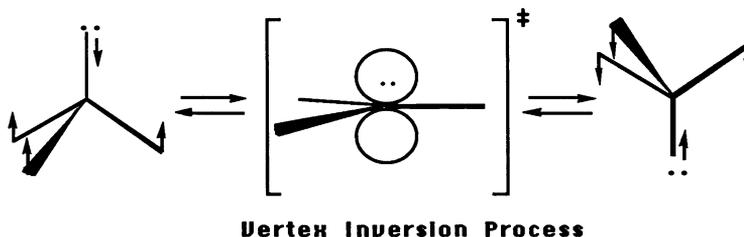
The chemistry of the ADPnO systems generally falls into two categories, one for phosphorus and a second for arsenic and antimony. For 10-P-3 ADPO oxidation generally results in the maintenance of a 10-electron bonding system although the coordination number is increased to form 10-P-5 systems. Action as a Lewis base causes a decrease in the number valence electrons involved in bonding at phosphorus and the formation of 8-P-4 systems. In contrast arsenic and antimony ADPnO systems are seen to increase both coordination number and electron count to afford 12-As-5 and 12-Sb-5 structures on oxidation. At arsenic and antimony centers action as a Lewis base generates 10-Pn-4 centers so that the coordination number is increased without a decrease in the number of valence electrons at the pnictogen center.



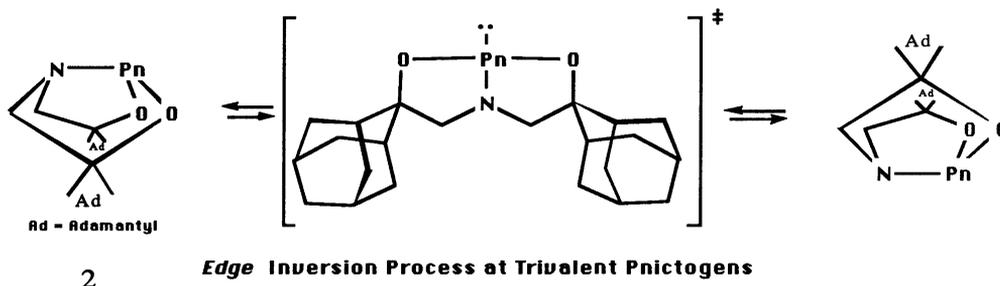
The potential *electromorphism* in the ADPnO systems also serves to suggest the planar 10-Pn-3 structure as a model for a transition state in a previously unrecognized inversion mechanism for tricoordinate pnictogens. This new *edge* inversion mechanism (ref. 4) differs from the classical (*vertex*) inversion found in nitrogen systems so that the geometric and electronic factors which influence barrier height are altered. The pnictogen lone pair is not actually inverted by the *edge* mechanism although the structures are. In essence the *edge* inversion mechanism can be thought of as a pseudo-rotation at a pyramidal center.



Edge Inversion Process



A number of systems have been investigated computationally the activation energies calculated to reveal substituent effects and periodic trends for the *edge* inversion process. Sterically encumbered molecules derived from saturated ADPnO analogues (2) have provided convenient systems in which the *edge* inversion barriers can be measured directly. Direct experimental determination of activation parameters has been possible on range of compounds related to 2 and are in accord with theoretical expectations (ref. 5). In general the barrier to *edge* inversion decreases for electronegative substituents (π donating) and electropositive central atoms (ref. 6). These trends are exactly opposite to those found for the classical *vertex* inversion mechanism.



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