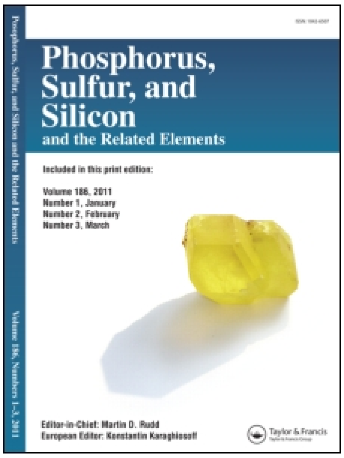

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The Chemistry of 10-Pn-3 Systems[1]: Tricoordinate Hypervalent Pnictogen Compounds and Related Systems

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THE CHEMISTRY OF 10-Pn-3 SYSTEMS[1]: TRICOORDINATE HYPERVALENT PNICTOGEN COMPOUNDS AND RELATED SYSTEMS.

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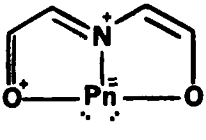
Abstract The unusual hypervalent tricoordinate pnictogen systems, 10-Pn-3 **ADPnO**, provide a convenient starting point for the study of a wide range of main group chemistry. Differences in reactivity patterns among the pnictogens are readily apparent from the variety of chemistry exhibited. The ADPnO systems also provide a model for the recently recognized edge inversion mechanism for 3 and 4 coordinate 8-electron main group species.

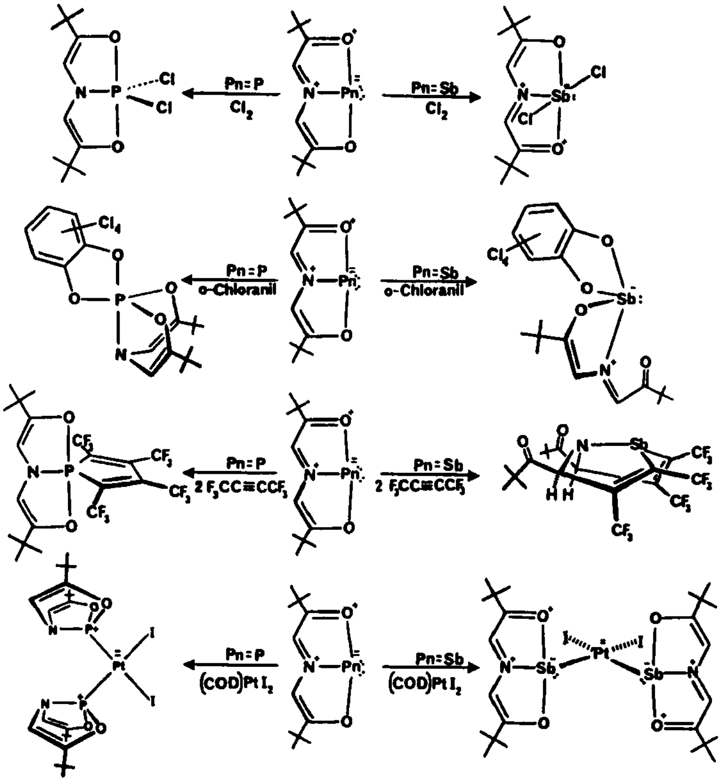
Transargononic compounds with low coordination about the hypervalent atom are uniquely useful in the study of hypervalent bonding systems. We have described the synthesis and structures of a family of 10-Pn-3 molecules (Pn=Pnictogen: N, P, As, Sb, Bi)[2]. The 10-Pn-3 **ADPnO** series represents the first stable 10-electron 3-coordinate pnictogen compounds.



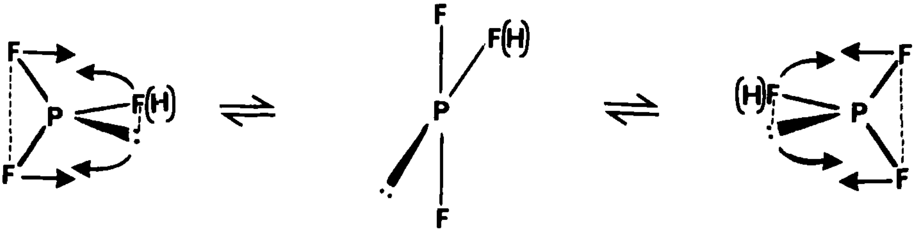
10-Pn-3 ADPnO

These ADPnO ring systems afford an opportunity to examine electromorphism[2a] between the "normal" 8-Pn-3 structures and the transargononic (hypervalent) 10-Pn-3 structures. At present we have observed the **ADPnO** ring system in both planar and bent arrangements. The geometry of the ring system correlates with the electronic demands on the pnictogen center.

Numerous derivatives of the **ADPnO** systems have been synthesized by reaction with halogens, addition of α-dicarbonyls, addition of acetylenes, oxidative insertions and transition metal complexation[2f]. The response of the pnictogen center to the action of the various reagents provides an indication of the types of bonding systems which can be supported by the differing pnictogen centers. In general phosphorus systems tend to show lower electron counts at the phosphorus center than their arsenic or antimony counterparts. Whereas phosphorus forms 8-P-4 and 10-P-5 structures, arsenic and antimony form 10-Pn-4 and 12-Pn-5 systems.

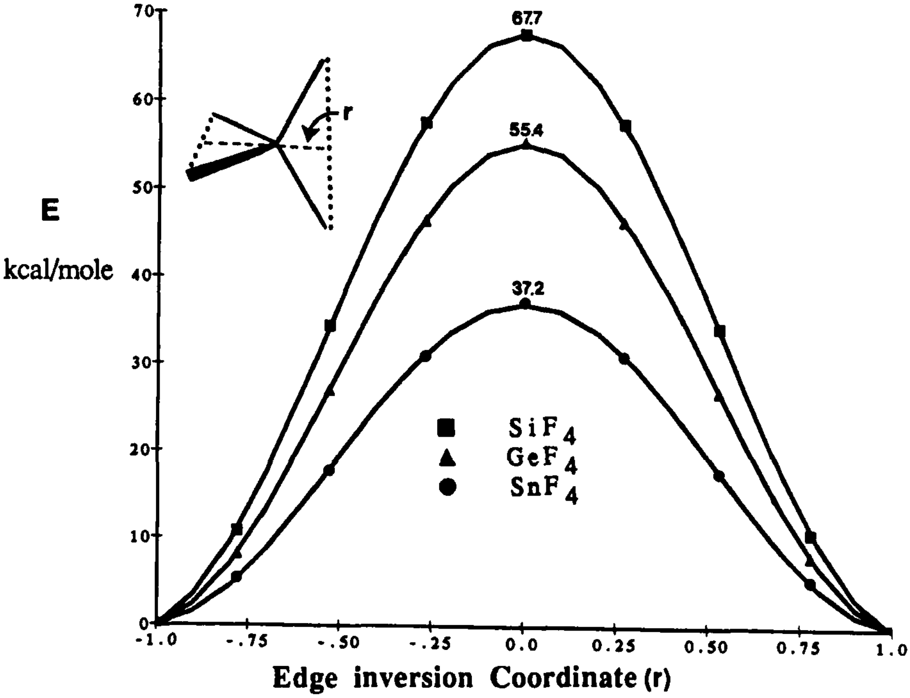


The planar 10-Pn-3 **ADPnO** structures can be viewed as a model for the transition state (or intermediate) for pyramidal inversion of tricoordinate pnictogens. This inversion takes place via an **edge** inversion process through a T-shaped transition state rather than the classical **vertex** inversion mode which proceeds through a planar trigonal transition state.



In the fluorophosphine series (PH_nF_{3-n}) PH_3 and PH_2F are predicted to invert by the classical **vertex** inversion mechanism while PF_2H and PF_3 are expected to invert by the **edge** inversion mechanism through a T-shaped transition state.[3] The transition states for PF_2H and PF_3 have been fully characterized computationally and are true transition states showing only one imaginary frequency which corresponds to the inversion mode. The direct measurement of a phosphorus **edge** inversion has been made on a saturated analog of **ADPO** and is in excellent agreement with theoretical expectations.[4]

The extension of this **edge** inversion mechanism to four coordinate group IV elements (Si,Ge,Sn) provides new insight into inversion through square planar transition states (the fourth substituent on the group IV elements replaces the lone pair in the pnictogen **edge** inversion process). All square planar transition states are fully characterized computationally and the reaction coordinate has been modeled with high level ab initio calculations.[5]



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