Table I. Slip Parameters[a] for $(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2$ (A) and $(\eta^3\text{-Cp})(\eta^5\text{-Cp})W(CO)_2$ (B)

complex	$\Delta = \lvert S \rvert$, Å	σ, deg	ψ, deg	ΔM–C
A, η^5-Ind	0.157	0.0	4.6	0.13
η^3-Ind	0.798	1.5	20.9	0.56
B, η^5-Cp	0.076	0.0	2.2	0.10
η^3-Cp	0.928	0.0	23.4	0.62

[a] Parameters are defined in ref 18 and 19. $\lvert S \rvert$ represents the slippage distance of the ring centroid from the projection of the metal atom on the ring, σ is the angle between the S vector and the vector from the ring centroid to the unique "allyl" carbon, ψ is the angle between the normal to the plane and the centroid–metal vector, and ΔM–C is the difference between the average of the metal carbon distances to the "allyl" and "ene" carbons.

V–C(2) = 2.237 (3) Å, V–C(3) = 2.272 (3) Å, while V–C(4) = 2.386 (3) Å and V–C(9) = 2.388 (3) Å. Faller, Crabtree, and Habib[18] have compared slippage parameters for known indenyl and cyclopentadienyl structures. Slip parameters for A and $(\eta^3\text{-Cp})(\eta^5\text{-Cp})W(CO)_2$,[18] B, are compared in Table I. Complex A represents a less extreme case than B but shows significantly more slippage than known η^5-systems ($\Delta < 0.3$).[18]

Even though complex A is expected to be more crowded than the isostructural tungsten[5] species, distortion of the η^3-Ind group from planarity is small. The dihedral angle between the η^3-carbons and the remaining carbon atoms of the η^3-Ind group for A is 12.0 (3)° in contrast to that of 26° for[5] $(\eta^3\text{-Ind})(\eta^5\text{-Ind})W(CO)_2$ or 28° for[8] $(\eta^3\text{-Ind})Ir(PMe_2Ph)_3$. Similar to these structures, the apex atom, C(11), of the η^3-fragment is 0.2 Å closer to the metal than the remaining carbons. Distances from the η^3-fragment to V(II) in this complex are shorter (by ~0.08 Å) than in $(\eta^3\text{-Ind})(\eta^5\text{-In})W(CO)_2$.[5] Two of the V–C(allyl) distances are equivalent to those in $(\eta^3\text{-Ind})Ir(PMe_2Ph)_3$; however, the apex atom in the Ir system is only 2.047 (8) Å from the metal. The greater planarity of the indenyl ring in A, the reduced value of Δ, and the long, but perhaps weakly interacting V–C(13) and V–C(18), distances suggest that the ene portion of the η^3-ring donates weakly to vanadium thereby reducing the electron deficiency at the 17-electron center. If the unpaired electron is localized toward the ene fragment then a 3-center-3-electron bond may begin to form analogous to the 2-center-3-electron bond postulated[11h] to explain the facile associative substitution pathway in 17-electron carbonyl complexes.

These results provide crystallographic evidence that first-row metals can support the slipped η^3-structure that has previously been structurally characterized for 18-electron complexes of heavier metals. For the first time ring slippage has been shown for a metal radical. These results further suggest that the 17-electron systems Cp_2VCO and $(\eta^5\text{-}C_5Me_5)_2VCO$, which substitute CO by a bimolecular process, may involve a 17-electron transition state or intermediate that contains a slipped ring. The question of whether 19-electron intermediates or 17-electron intermediates containing a slipped η^3-ring (or both) are present in reactions of metal cyclopentadienyl radicals remains to be answered.

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Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic temperature factors, hydrogen atom coordinates, and calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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A New Inversion Process at Group V (Group 15)† Elements. Edge Inversion Through a Planar T-Shaped Structure

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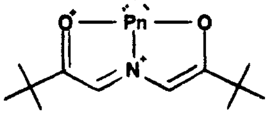
We report a new mechanism for inversion of tricoordinate pyramidal pnictogens, 8-Pn-3 (Pn = P, As, Sb). Classical inversion of these species is believed to proceed through a trigonal-planar transition state. The recent synthesis[1-3] of molecules containing a planar T-shaped pnictogen (**1**) suggests that similar geometries could be involved in inversions at some 8-Pn-3 centers.



1

The classical inversion barrier at pyramidal phosphorus is expected to be quite high with electronegative substituents. The inversion barrier in PH_3 is calculated as 42.1 kcal/mol with a double-ζ + d(P) basis set, whereas the barrier for PH_2F is calculated as 62.1 kcal/mol.[4a] Calculations on planar D_{3h} PF_3 reveal that the lone pair is not in a 3p orbital (a_2'') but rather is in an a_1' orbital with a 3s component.[4b,5] On the basis of ab initio calculations described below, we propose that with appropriate electronegative substituents, the pyramidal phosphorus species (and by analogy heavier pnictogens) will invert through an approximate T-shaped transition state (or intermediate).

Calculations were performed at the SCF level[6] with a polarized double-ζ basis set.[7] All geometries were gradient-optimized in the appropriate symmetry.

Calculations were done for the successive fluorination of phosphine: PH_3, PH_2F, PHF_2, PF_3. The optimum geometries for the pyramidal (A), planar "D_{3h}" (B), and planar "T-shaped" (C) structures are given in Table I. Our calculated structures are in good agreement with the experimental geometries for pyramidal PH_3, PHF_2, and PF_3.[8-10] Good agreement for the py-

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† In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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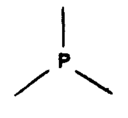
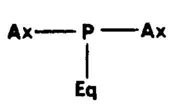
A

(C_s or C_{3v})



B

(C_{2v} or D_{3h})



C

(C_{2v})

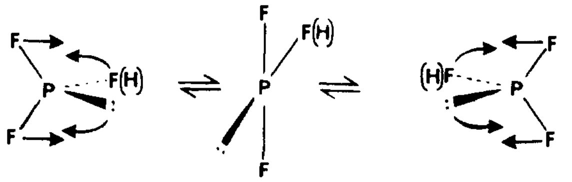
ramidal structures (A) is also found with the calculations of Boggs and co-workers.[4a] We also find good agreement for the structures of the classical inversion transition states B except for PF_3 where Boggs and co-workers[4a] placed the lone pair in an a_2'' orbital. Comparison of the pyramidal A and planar B structures (excluding PF_3) shows that the bond lengths decrease in going from the pyramidal to planar structures in agreement with previous observations.[11] For PF_3, the bond length in structure B increases which is consistent with the lone pair occupying an in-plane a_1' orbital.

The planar T-shaped structures C show novel features. For PH_2F and PHF_2 C_{2v} symmetry was maintained and thus the hydrogens are in the axial positions in the former and fluorines are in the axial positions in the latter. In all cases, the three ligands optimize to the same side of the phosphorus (the axial substituents are bent back toward the equatorial substituent). As expected the axial substituents have long bond lengths. For example, in PH_2F (C), the P–H bond is 13.1 pm longer than in structure A and 17.8 pm longer than in structure B. The P–F equatorial bond in PH_2F (C) is slightly longer, 0.5 pm, than in B but is shorter by 1.0 pm as compared to A. The axial P–H bonds in PH_3 (C) are even longer, 24.1 pm, as compared to PH_3 (A) while the equatorial P–H bond is shorter by 0.5 pm as compared to A. The axial P–F bonds in C for PHF_2 and PF_3 show a less dramatic lengthening of 7.0 pm. For PF_3 (C) the equatorial P–F bond is 8.0 pm shorter than the axial P–F bonds.

The barriers for inversion through B are slightly lower (excluding PF_3) than those reported by Boggs and co-workers[4a] (Table I). The classical inversion barriers through a B structure increase as F is substituted for H as previously observed.[4a] Our value for PH_3 is only 1 kcal/mol above that calculated with a DZ + P basis set of STO's.[11] Our value for PF_3 (B) is essentially the same (3.4 kcal/mol higher) as Marynick's value[5] (a_1' HOMO).

Phosphine will invert through structure B as structure C is 121.2 kcal/mol higher in energy than structure B. For PH_2F, structure C is still 67.2 kcal/mol above structure B and clearly PH_2F will invert via a classical planar structure. However, structure C for PHF_2 is 35.6 kcal/mol below structure B, and for PF_3, structure C is 56.2 kcal/mol below structure B. Thus PHF_2 and PF_3 will invert through a T-shaped structure C but not via a classical planar-trigonal structure B.

The inversion process may be visualized as the one involving simple angle deformation motions (eq 1). For PHF_2 and PF_3, the T-shaped structure C can arise from a pyramidal configuration by simultaneous opening of the F–P–F and F(H)–P–lone pair angles. Microscopic reverse of the process can occur in two degenerate ways and provides A or its inverted structure.



(1)

A C A

Table I. Optimized Geometry Parameters[a] and Inversion Barriers[b] for Fluorinated Phosphines

property	PH_3	PH_2F	PHF_2	PF_3
r(PH) A	140.7	140.8	140.9	
r(PF) A		160.2	158.1	156.3
θ(APA) A	95.2	94.1	98.5	97.1
θ(HPF) A		98.1	96.3	
r(PH) B	137.1	136.1	135.2	
r(PF) B		158.7	157.1	166.4
θ(APA) B	120.0	131.2	109.6	120.0
θ(HPF) B		114.4	125.2	
r(PH) C	164.8 (ax) 140.2 (eq)	153.9 (ax)	139.7 (eq)	
r(PF) C		159.2 (eq)	165.5 (ax)	155.3 (eq) 163.3 (ax)
θ(axPax) C	166.0	158.0	168.0	172.8
θ(axPeq) C	83.0	79.0	84.0	86.4
barrier (B)	37.9	59.5	101.6	124.9
HOMO (B)	a_2''	a_2''	a_2''	a_1'
barrier (C)	159.1	126.7	66.0	68.7

[a] Bond distances in pm; Bond angles in degrees: ax = axial; eq = equatorial. [b] Inversion barriers (geometry of planar structure) in kcal/mol.

Throughout the process the lone pair remains on the same face of the P and electronic repulsions between the lone pair and the ligands' electrons are kept minimum. By contrast, such electron repulsions significantly increase in the classical process involving structure B that inverts the lone pair through the plane. Inversion via structure C amounts to edge inversion of a tetrahedral structure through a square-planar species, whereas the classical inversion through a planar-trigonal species B represents face or vertex inversion.

The accessibility of the planar T-shaped structure not only should allow for a new process for changing conformation at pnictogen centers but also suggests a plausible explanation for the stability of compounds such as **1**. Experimental demonstration of this novel inversion process and studies of factors that influence relative energies of structure A, B, and C are in progress.

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Structure of a Metalated Schiff Base[1]

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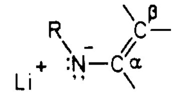
1-Azaallyllithium reagents **1** have aroused widespread interest because of their synthetic utility and fascinating aspects of (stereo)isomerism. Whereas the problem of *E/Z* isomerism about the CαCβ double bond appears to be provisionally settled,[3-6] exploration of the CαN configuration of **1** had to rely on more



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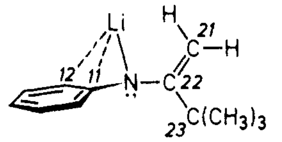

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