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Theoretical Data on the Multicoordination of Phosphorus and Arsenic

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Abstract: Some multicoordinate model compounds of phosphorus and arsenic are investigated by ab initio effective potential calculations at both SCF and CI levels. Structures and relative stabilities of the species MX_3, MX_4^+, MX_4^-, MX_5, and MX_6^- are reported for M = P, X = H and Cl, and M = As, X = H. The Lewis acid properties of phosphoranes and arsoranes (MX_5) are shown. The barrier to Berry pseudorotation is calculated at 2.0 kcal/mol for PH_5 and 2.5 kcal/mol for AsH_5. Within their respective series, arsoranide AsH_4^- appears relatively more stable than phosphoranide PH_4^-. Two possible pathways for isomerization of hexacoordinate phosphorus compounds are compared; the easier way appears to occur through a bond rupture.

I. Introduction

An important difference between the first and subsequent rows of the main-group elements is the ability of the latter to be involved in hypervalent molecules. Hypervalence was first seen as the structural consequence of mixing *n*s and *n*p valence atomic orbitals (AO's) with *n*d valence AO's, giving hybrids such as sp^3d in PCl_5 and sp^3d^2 in PCl_6^-. However, theoretical studies always show a very small occupation of the d valence AO's for these molecules. Consequently another model, namely the formation of three-center four-electron (or electron rich) bonds, was presented to explain the violation of the octet rule in hypervalence.[2]

The elements of group 5B provide a good example of hypervalence. Nitrogen does not form hypervalent molecules whereas hypervalent phosphorus compounds are stable and common (e.g., phosphoranes PR_5).

There are other ways to characterize the state of an atom in a given environment; these are (i) the oxidation number (more formal and less useful for non-metal main-group atoms), (ii) the number of electrons shared by the atom,[3] and (iii) the coordination number. The last concept only considers the number of neighbors linked to the studied atom. For instance, there are various compounds in which a phosphorus atom is mono-, di-, tri-, tetra-, penta-, or hexacoordinate. This nomenclature appears to be non-ambiguous, and for this reason we shall use it in this work.

There have been many theoretical studies on group 5B hypervalent molecules, mainly those involving phosphorus.[4-13] The primary object of this work was to give energetic information on the stability of hexacoordinate phosphorus compounds through ab initio calculations. Only the systems in which phosphorus shares 12 electrons, such as PCl_6^-, are considered here. Such systems are known, and questions arise about their formation from pentacoordinate derivatives and about their isomerization.[14,15] The specific case of tris-chelate derivatives was also studied experimentally in our group.[16]

In this work, we have computed the relative stabilities of the various species PX_3, PX_4^+, PX_4^-, PX_5, and PX_6^-. First, we studied the models in which X = H, for which we included the correlation effects in our calculations. Some theoretical data were already available on these models (such as for the reaction $PH_3 + H_2 \rightarrow PH_5$),[13] which we treated again for the sake of consistency. Second, we have considered the real molecules with X = Cl for which some structural and thermodynamic data are available. Last, we performed similar investigations on arsenic by carrying out calculations on the AsH_n models. Although the multicoordination chemistry of arsenic is less developed than that of phosphorus, differences between the chemical behavior of these two atoms, some concerning the preferred coordination, have been pointed out.[17-21] Additionally, the calculated barriers to Berry pseudorotation are reported for PH_5 and AsH_5.

The calculations on these relatively "heavy" molecules were made possible by use of pseudopotential techniques which allow explicit treatment of only valence electrons in the calculations. Thereby reliable valence basis sets could be used and configuration interactions (CI) could be carried out on the PH_n and AsH_n systems.

II. Computational Means and Basis Sets

The ab initio valence-only SCF + CI calculations were performed by using the pseudopotential method of Durand and Barthelat.[22] The SCF program is the HONDO package[23] modified by one of us (J.P.D.) to include pseudopotential and named PSHONDO program. The performance of this pseudopotential technique has been tested by many calculations on molecules containing second- and third-row atoms.[24-30] The present cal-

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Table I. SCF Calculated Geometries for PH_n, AsH_n, and PCl_n Systems[a]

molecules	symmetry	parameters	PH_n	AsH_n	PCl_n
MX_3	C_{3v}	*a*	1.416 (1.420)	1.527 (1.520)	2.101, 2.055[b] (2.043)
		α	95.4 (93.3)	94.3 (92.0)	100.0, 100.6 (100.1)
MX_4^+	T_d	*a*	1.397 (1.42)[c]	1.497	2.001 (1.98)[c]
MX_4^-	C_{2v}	*a* (ax)	1.716	1.845	2.467
		b (eq)	1.409	1.523	2.125
		α	165.6	164.6	185.2
		β	102.8	100.1	99.8
MX_5	D_{3h}	*a* (ax)	1.478	1.612	2.211 (2.12)[d]
		b (eq)	1.418	1.528	2.063 (2.02)[d]
MX_6^-	O_h	*a*	1.494	1.620	2.219 (2.07)[c]
MX_6^-	D_{3h}	*a*	1.519		2.308
		α	82.2		79.8
H_2		*a*	0.748 (0.741)		
Cl_2		*a*			2.146 (1.988)

[a] In Å and deg. The parameters are defined in Figure 1. When available, experimental values are given in parentheses (from ref 35 when non-precized). [b] With d functions on chlorine. [c] Reference 36a. [d] Reference 36b.

culations also provide reliable comparisons with all-electron ab initio studies.

For chlorine and phosphorus atoms, a four primitive Gaussian basis set has been optimized in pseudopotential Hartree–Fock (HF) calculations and then contracted to a double-ζ basis. For phosphorus a 3d polarization orbital ($\eta_d = 0.57$) was added, taken from ref 13 and corresponding to the optimum value of PH_3. For chlorine, one additional s orbital ($\eta_s = 0.058$) and p orbital ($\eta_p = 0.043$) were optimized in pseudopotential HF calculations on Cl^-, leading to a calculated electron affinity (2.63 eV) in good agreement with the near-HF all-electron value (2.58 eV).[31] This basis set for chlorine was completed by a 3d polarization function ($\eta_d = 0.63$) for test calculations on PCl_3 (see section IV). The hydrogen basis set is a 4s Huzinaga[32] basis augmented by a flat s orbital ($\eta_s = 0.03$) and polarization p orbital ($\eta_p = 0.65$) taken from basis set C of ref 13.

For the phosphorus and arsenic hydrides PH_n and AsH_n, correlation energy calculations were performed with the CIPSI method[33,34] in which a multideterminantal wave function is built upon the most important determinants. This zeroth-order description is then improved through the second-order Rayleigh–Schrödinger perturbation theory. All determinants whose coefficients in the first-order perturbed wave function are greater than a given threshold are included in the reference space in the next step; the process may be iterated up to the desired precision. In the current calculations, the threshold was fixed to 0.02 which corresponds to a dimension for the reference space ranging from 20 to 35 determinants.

III. PH_n Systems

A. Structures. The geometrical structures calculated in this work are all reported in Figure 1 and Table I. For PH_n molecules, our computed structures are in good agreement with the previous all-electron results as long as the valence basis sets are comparable.[11,13] PH_4^-, which is a 10-electron (on phosphorus) entity, has a C_{2v} structure as expected from the VSEPR model. the C_{4v} square-pyramidal form (P–H = 1.473 Å; ∠HPH = 103.3°) is calculated to be 9 kcal/mol higher than the C_{2v} form (SCF level). This value is not necessarily the barrier for Berry pseudorotation of PH_4^- since the transition state for the pseudorotation of a PR_4^- system does not necessarily have a C_{4v} symmetry, **1**.

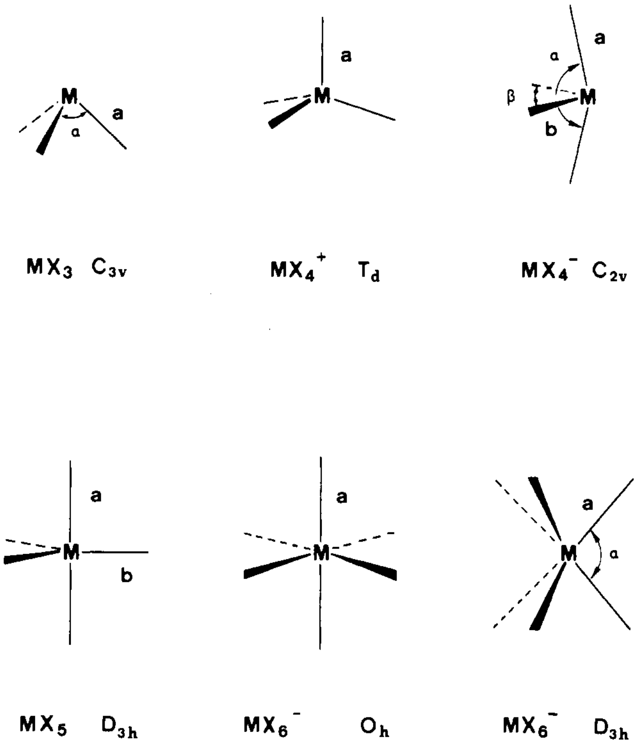

Figure 1. Definition of the geometrical parameters given in Table I.

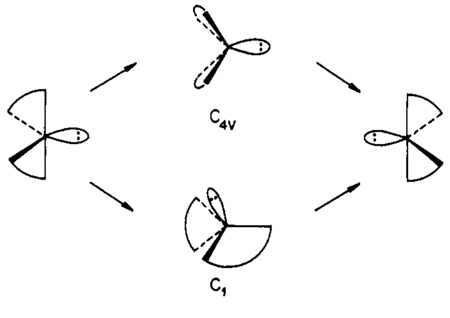

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Table II. Mulliken Population Analyses

	net atomic charges			d population on P or As	calcd dipole moment,[a] D
	P or As	H	Cl		
PH_3	+0.21	−0.07		0.09	0.97 (0.58)
PH_4^+	+0.68	+0.08		0.12	
PH_4^-	+0.20	−0.60 ax 0.00 eq		0.14	0.58
PH_5	+0.66	−0.21 ax −0.08 eq		0.26	
PH_6^-	+0.68	−0.28		0.34	
AsH_3	+0.21	−0.07		0.10	0.42 (0.20)
AsH_4^+	+0.60	+0.10		0.12	
AsH_4^-	+0.24	−0.58 ax −0.04 eq		0.16	1.12
AsH_5	+0.68	−0.25 ax −0.06 eq		0.26	
AsH_6^-	+0.86	−0.31		0.35	
PCl_3	+0.39		−0.13	0.18	1.80
PCl_3[b]	+0.51		−0.17	0.20	0.98 (0.78)
PCl_4^+	−0.12		+0.28	0.36	
PCl_4^-	+0.58		−0.63 ax −0.16 eq	0.16	1.69
PCl_5	+0.03		−0.21 ax +0.13 eq	0.35	
PCl_6^-	+0.14		−0.19	0.33	
PCl_6^- (D_{3h})	+0.38		−0.23	0.24	

[a] Experimental values in parentheses, from ref 38. [b] With d functions on chlorine.

The C_{4v} geometry of PH_5 has also been calculated and is reported later in this work (the discussion about Berry pseudorotation in PH_5 and AsH_5).

The PH bond lengths are in the range 1.40–1.42 Å except for axial bonds in PH_5 and PH_4^- and bonds in PH_6^-. In PH_4^- the axial bonds are particularily long (1.72 Å). This can also be noticed in PCl_4^- and AsH_4^-.

PH_6^- in which phosphorus bears 12 electrons, as sulfur does in SH_6,[9] has an octahedral geometry as expected also from the VSEPR model. The D_{3h} structure is found to be much less stable. The PH bond in $PH_6^-(O_h)$ is slightly longer than the axial PH bond in PH_5. In $PH_6^-(D_{3h})$, the PH bond is even longer, possibly due to the repulsion between the $H^{-\delta}$'s. Our calculated O_h and D_{3h} geometries for PH_6^- are in agreement with MINDO/3 results.[37]

The Mulliken population analyses are reported in Table II. PH_4^- bears its negative charge mainly on the axial hydrogens. In PH_6^- (both O_h and D_{3h}) the negative charge is pushed toward the hydrogen atoms so that phosphorus remains as positive as in PH_4^+. This withdrawing of electrons may be due to our rich basis set for hydrogen. However, a deeper inspection of Table II shows that the central atom charges fall into two groups: a set of values (~0.2) for PH_3 and PH_4^- and a larger but nearly constant set of values for PH_4^+, PH_5, and PH_6^-. This can be accounted for by a similar hybridization in PH_3 and PH_4^-, both of which possess a single lone pair.[39]

Table III. Calculated Reaction Energies for PH_n Systems

reactions	ΔE,[a] kcal/mol	
	SCF	CI
$PH_3 + H^+ \rightarrow PH_4^+$	−197.3	−194.6
$PH_3 + H^- \rightarrow PH_4^-$	+4.8	+1.4
$PH_3 + H_2 \rightarrow PH_5$	+45.0	+45.0
$PH_3 + 2H \rightarrow PH_5$	−36.6	−58.9
$PH_4^+ + H^- \rightarrow PH_5$	−160.4	−166.9
$PH_4^- + H^+ \rightarrow PH_5$	−362.5	−361.8
$PH_4^- + H_2 \rightarrow PH_6^-$	+10.8	+10.7
$PH_5 + H^- \rightarrow PH_6^-$	−29.4	−31.7
$PH_6^- + PH_4^+ \rightarrow 2PH_5$	−131.0	−135.2
$PH_6^- \rightarrow PH_6^{-*}(D_{3h})$	+58.9	+55.2

[a] ΔE is the difference between total energies of reactants and products without taking into account the zero-point vibration energies. A negative sign means the product (right member) is more stable.

As has been shown many times, the occupation of d AO's remains weak even for the formally sp^3d- and sp^3d^2-hybridized species (see Table II).

B. Energetics. We report in Table III the SCF and CI calculated energy ΔE for some reactions. ΔE corresponds to ΔH°(gas), neglecting the difference in zero-point vibration energies. The CI results modify only slightly the values calculated at the SCF level.

The gas-phase proton affinity of PH_3 was experimentally determined at 188 kcal/mol.[40] Our calculated value is 7 kcal/mol greater. PH_4^- is not bound with respect to $PH_3 + H^-$, but the CI reduces the corresponding energy difference to a small value. The SCF calculated energy difference $PH_3 + H_2/PH_5$ is in good agreement with the corresponding value calculated by Kutzelnigg et al. (43 kcal/mol).[13] Concerning the effect of the CI, we found a negligible influence whereas these authors found that the CI (CEPA method) lowers this value by 4 kcal/mol.

Due to the strength of the H_2 bond, PH_5 is not stable with respect to $PH_3 + H_2$ while it is stable with respect to $PH_3 + 2H$. Similarily PH_6^- is not stable with respect to $PH_4^- + H_2$, while it is stable with respect to $PH_5 + H^-$. Dismutation of $2PH_5$ to $PH_6^- + PH_4^+$ is unfavorable. For these two reactions, our energy values agree with the SCF values reported by Kutzelnigg.[13]

As expected $PH_6^-(D_{3h})$ is less stable than $PH_6^-(O_h)$. The SCF energy difference (59 kcal/mol) is much higher than the difference predicted by semiempirical calculations on PH_6^- (41 kcal/mol, CNDO; 15 kcal/mol, MINDO/3),[37] but it is less than the energy difference between $SH_6(O_h)$ and $SH_6(D_{3h})$ calculated at the SCF level (97 kcal/mol, STO-3G; 101 kcal/mol, STO-3G+d).[9]

IV. PCl_n Systems

A. Structures. PCl_3 was chosen to test the influence of d AO's in the chlorine basis set on the SCF calculated geometry. As can be seen in Table I, the d AO's on chlorine are required to obtain a correct geometry for PCl_3.[41] Nevertheless, to reduce the size of the basis sets and computing time for the other PCl_n moelcules, the d functions were not included in the chlorine basis set. Most probably this explains the excessive length of our calculated P–Cl bond lengths when compared with test results (see Table I). Our overestimation is 0.02–0.09 Å except for PCl_6^- where the desagreement is more severe (0.15 Å). The trend within our calculated values is, however, consistent.

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(39) This explanation, which holds also for the arsenic hydrides AsH_n, has been suggested by a referee. Bonding in second- and third-row main-group elements is dominated by large s–p gaps. To avoid hybridization, lone pairs keep s character and the bonding orbitals involve mainly p contributions. Therefore the nature of hybridization is similar in PH_3 and PH_4^-. In PH_4^- the weak axial bonds could be schematically constructed with a three-center four-electron bond by using one phosphorus p orbital. In the remaining systems PH_4^+, PH_5, and PH_6^-, phosphorus bears no lone pair and more hybridization is required. Actually d orbitals are more populated in XH_5 and XH_6^- species (see Table II).

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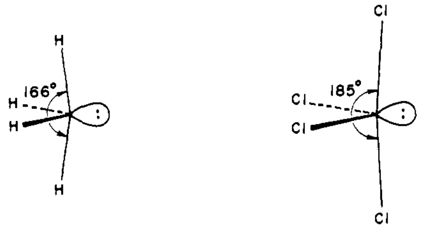
Table IV. Calculated Reaction Energies for PCl_n Systems

reactions	ΔE(SCF),[a] kcal/mol
$PCl_3 + Cl_2 \rightarrow PCl_5$	+3.1
$PCl_3 + Cl^- \rightarrow PCl_4^-$	-18.9
$PCl_4^+ + Cl^- \rightarrow PCl_5$	-122.0
$PCl_4^+ + 2Cl^- \rightarrow PCl_6^-$	-158.6
$PCl_4^- + Cl_2 \rightarrow PCl_6^-$	-14.7
$PCl_5 + Cl^- \rightarrow PCl_6^-$	-36.6
$PCl_6^- + PCl_4^+ \rightarrow 2PCl_5$	-85.4
$PCl_6^- \rightarrow PCl_6^{-*}(D_{3h})$	+64.6

[a] Same comments as in Table III.

The calculated C_{2v} structure for PCl_4^- shows the following peculiarity. The axial angle ClPCl is 185°. This contrasts with the calculated structure for PH_4^-, **2**. Attempts to prepare PCl_4^- have failed,[42] but the ion PBr_4^- has been prepared and its crystal structure has been determined.[43] The ion has a C_{2v} structure with an axial angle ∠BrPBr of 170° across the lone-pair side of the structure. This would correspond to a 190° angle in **2** (α in Figure 1), agreeing with our "open" angle in PCl_4^-. This suggests a less stereospacial lone pair in such compounds. Indeed, in PCl_4^- the negative charge is distributed all over the chlorines, including the equatorial ones (see Table II), possibly inducing repulsions between equatorial and axial atoms.[44]



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The Mulliken population analyses show polarizable P–Cl bonds. This appears, for instance, through the difference in charge distribution between $PCl_6^-(O_h)$ and $PCl_6^-(D_{3h})$ (for PH_6^-, the net charges are identical for both geometries).

B. Energetics. Some SCF reaction energies involving PCl_n systems are reported in Table IV. Corrections due to the CI could be extrapolated from the results on PH_n, but these effects were shown to be minor.

PCl_5 was calculated at 3 kcal/mol above ($PCl_3 + Cl_2$). This is in contradiction with other experimental results[45] and could be due to our basis set or, in this isolated case, the CI could have stabilized the PCl_5 form. PCl_5 is known to exist under trigonal-bipyramidal neutral molecules in vapor phase,[46] in molten states, and in most non-ionizing solvents. In the solid state PCl_5 is [PCl_4^+, PCl_6^-],[47] and in solution in polar solvents PCl_5 undergoes two competing equilibria:[48]

$$2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^- \tag{1}$$

$$PCl_5 \rightleftharpoons PCl_4^+ + Cl^- \tag{2}$$

Our calculated energetics of course refer to gas-phase species. According to our results, dismutation reaction 1 requires 85 kcal/mol (SCF level) and heterolytic dissociation reaction 2 (which can be seen as the first step in dismutation (eq 1)) requires 122 kcal/mol (SCF level). In the solid state, the stabilizing energy due to the Madelung field overcompensates easily the loss of energy required by the dismutation of $2PCl_5$. In ionizing (i.e., polar) solvents, the solvation of each ionic species PCl_4^+, PCl_6^-, and Cl^- brings the stabilizing energy required by the dissociation (eq 2) and a fortiori by the dismutation (eq 1).

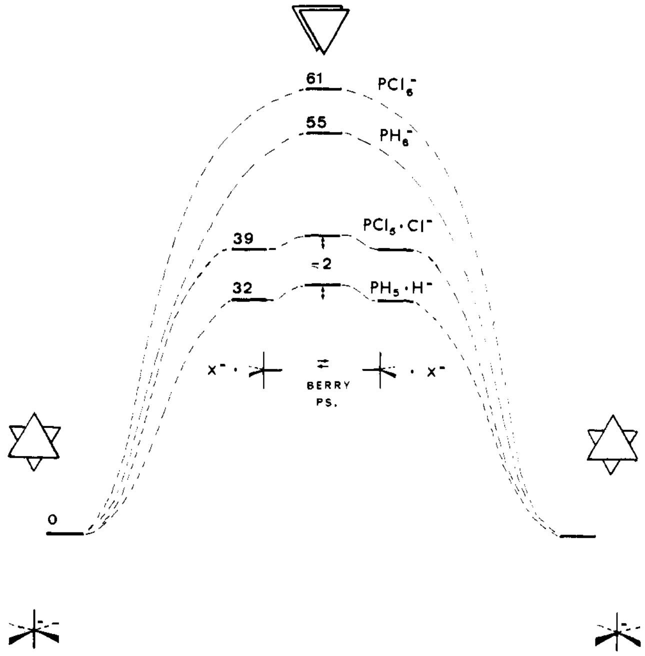

Figure 2. Calculated energies (in kcal/mol) of the two pathways for isomerization of PH_6^- and PCl_6^-.

PCl_4^- is bound with respect to ($PCl_3 + Cl^-$). PCl_6^- is more stable than ($PCl_4^- + Cl_2$) and is bound with respect to ($PCl_5 + Cl^-$). The stabilization of the hexacoordinate form with respect to the pentacoordinate form is comparable for PCl_5 and PH_5. On the other hand, the dismutation (or autoionization) of PCl_5 (eq 1) demands less energy than that of PH_5 (131 kcal/mol at the SCF level). D_{3h} PCl_6^- is high in energy with respect to its O_h equilibrium geometry. A general trend that appears in Table IV is the good stability of PCl_6^- and the poor stability of PCl_4^+.

Jenkins et al.[49] have reported thermodynamic data on some gas-phase processes involving PCl_4^+ and PCl_6^-. Even if we use estimates of CI effects from Table III, our calculated ΔE's are not in quantitative agreement with their calculated ΔH's:

	ΔH,[49] kcal/mol	ΔE, kcal/mol
$PCl_4^+ + 2Cl^- \rightarrow PCl_6^-$	-203	-167
$PCl_5 + Cl^- \rightarrow PCl_6^-$	-62	-39
$PCl_4^+ + Cl^- \rightarrow PCl_5$	-141	-129

V. Pathways for Isomerization of Hexacoordinate Phosphorus Compounds

The chiral phosphorus(VI) compounds such as tris-chelate anions give rise to enantiomeric isomerism **3**.[15,16] Two mechanisms have been suggested for this isomerization: (1) a mechanism with bond rupture giving a pentacoordinate phosphorane and then a

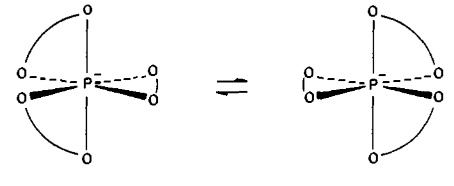

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Table V. Calculated Reaction Energies for AsH_n Systems

reactions	ΔE,[a] kcal/mol SCF	CI
$AsH_3 + H^+ \rightarrow AsH_4^+$	−190.0	
$AsH_3 + H^- \rightarrow AsH_4^-$	−2.2	−6.3
$AsH_3 + H_2 \rightarrow AsH_5$	+58.2	+58.6
$AsH_4^+ + H^- \rightarrow AsH_5$	−154.5	
$AsH_4^- + H^+ \rightarrow AsH_5$	−342.3	−340.5
$AsH_4^- + H_2 \rightarrow AsH_6^-$	+27.7	
$AsH_5 + H^- \rightarrow AsH_6^-$	−32.6	
$AsH_6^- + AsH_4^+ \rightarrow 2AsH_5$	−121.9	

[a] Same comments as in Table III.

Berry pseudorotation and closure to the other hexacoordinate isomer and (2) a direct trigonal twist mechanism without bond rupture, through a prismatic D_{3h} transition state.

Our results (see Tables III and IV)[50] show that the dissociative route is much more probable than the direct twist mechanism. This is in qualitative agreement with semiempirical calculations on PH_6^- and PF_6^- [37] and with ab inition calculations on SH_6.[9] We therefore support the bond-rupture mechanism. The energetic pathways for the models PH_6^- and PCl_6^- are summarized in Figure 2. Experimental results plead in favor of this nondirect mechanism. Observed $\Delta G^{\ddagger}$ for such isomerizations of spirophosphoranes span from 14 to 21 kcal/mol.[15,16] We think our models allow a choice between the two mechanisms. However, we cannot predict accurate ΔH values for the real complex systems; on the other hand the entropic terms ΔS were found to be of importance in these reactions. In any case, the PR_6^- systems have a nonflexible structure, unlike the PR_5 systems, agreeing with the experimental results of Caruana et al.[16]

VI. AsH_n Systems

A. Structures. Calculations on mocel AsH_n molecules were carried out partly because our attention was drawn[17-21] to a certain stability of arsoranides AsR_4^- whereas in the phosphorus series the phosphoranes are very common and the phosphoranides are more unstable. A previous work has established the reliability of our arsenic pseudopotential as far as structures and energetics are concerned.[51] The SCF-calculated geometry of AsH_3 given in Table I reproduces correctly the known geometry of AsH_3. The calculated structures for AsH_n models given in Table I are interesting since, to date, few ab initio calculations on arsenic compounds are available.[52]

Table I shows a great similarity between the structures of the AsH_n molecules and those of the PH_n molecules. As a whole the As–H bonds are 0.1 Å longer than the P–H bonds. Another similarity between PH_n and AsH_n molecules appears in the Mulliken population analyses displayed in Table II. Net charges and d populations are pretty much the same on phosphorus and arsenic atoms with an exception in AsH_6^- where As bears a net charge of +0.86 (vs. +0.68 on P in PH_6^-).

B. Energetics. Table V reports the calculated reaction energies for some AsH_n systems. The CI is included only for some important points; its effects are nearly the same as those occurring in the PH_n systems.

No experimental value is available for the gas-phase proton affinity of arsine AsH_3; we predict a value of ≈180 kcal/mol. AsH_4^- is bound with respect to AsH_3 and H^-. This is a significant difference between arsenic and phosphorus. Moreover, this result agrees with experimental evidence[17-21] for the stability of certain arsoranides AsR_4^- while phosphoranides PR_4^- are very unstable.[53]

Table VI. Results on Berry Inversion in PH_5 and AsH_5

		PH_5	AsH_5
C_{4v} geometry[a]	XH basal	1.453	1.577
	XH apical	1.402	1.506
	$\angle H_{bas}XH_{ap}$	100.4	101.2
Barrier[b] ΔE =	SCF	2.8	3.2
$E_{C_{4v}} - E_{D_{3h}}$	CI	2.0	2.5

[a] In Å and deg. [b] In kcal/mol.

Table VII. Selected stretching force constants, in mdyn/Å

k_{P-H}		k_{As-H}		k_{P-Cl}		
PH_3	3.8	AsH_3	3.2	PCl_3	2.9	3.4[a]
PH_4^- ax	1.1	AsH_4^- ax	1.2	PCl_4^- ax	1.0	
PH_4^- eq	3.6	AsH_4^- eq	3.2	PCl_4– eq	2.5	
$PH_6^-(O_h)$	2.8	AsH_6^-	2.8	$PCl_6^-(O_h)$	3.0	
$PH_6^-(D_{3h})$	2.6			$PCl_6^-(D_{3h})$	2.0	

[a] With d functions on chlorine.

Another difference is the reduced relative stability of arsoranes AsH_5 when compared to the stability of phosphoranes. This appears in the demanded energy of the reaction $XH_3 + H_2 \rightarrow XH_5$ which is greater for arsenic than for phosphorus. The stabilization of the hexacoordinate forms with respect to the pentacoordinate forms is of similar magnitude for arsenic and phosphorus. However, with respect to ($XH_4^- + H_2$), XH_6^- is unbound by 28 kcal/mol when X = As and by only 11 kcal/mol when X = P, indicating again the stability of arsoranides.

C. Berry Pseudorotation in PH_5 and AsH_5. Kutzellnigg and Wasilewski[13] have clearly demonstrated that the mechanism of inversion in species such as PH_5 (D_{3h}) normally occurs through a Berry pseudorotation pathway via a square-pyramidal (C_{4v}) transition state. Therefore, a simple calculation of the relative energy of this C_{4v} transition state gives the barrier for Berry pseudorotation and inversion. For PH_5, the most refined calculations give a barrier of 2 kcal/mol.[13] We have investigated this C_{4v} transition state for both PH_5 and AsH_5. The results are reported in Table VI. As in the other species studied here, the geometries were optimized at the SCF level. For PH_5, the agreement is excellent with previous calculations for both geometry and energy.[13,54] In AsH_5 (C_{4v}), the relative changes in bond lengths are remarkably the same as in PH_5. We predict a barrier of 2.5 kcal/mol which is not very different from the barrier in PH_5. The corresponding barriers in PF_5 and in AsF_5 have been measured from Raman spectra.[55] They are in the same energy range although the barrier for AsF_5 is inferior to that of PF_5. Some spiranic derivatives are known to prefer a C_{4v} geometry over a D_{3h} one.[56] We think this presents no conflict with our results since the energy difference of 2.5 kcal/mol in our model can be easily counterbalanced by electronic effects, steric hindrances, or cycle strains.

VII. Discussion and Conclusion

Throughout this work we have given evidence for some energetic differences between phosphorus and arsenic multicoordinate compounds. As far as the structures are concerned, the two series of compounds are quite similar. This is also true for the calculated force constants (Table VII)[57] and orbital energy levels. Tables

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(50) In our calculations on PH_6^-, PCl_6^-, and AsH_6^- the constraints of symmetry O_h or D_{3h} are fixed. It can be verified in ref 37 that for such symmetrical 12 e species, the O_h and D_{3h} geometries correspond respectively to real minima and maxima (i.e., transition states) on the SCF hypersurface.

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(53) The analysis previously done for the PH_n systems (footnote 39)may be extended to account for the calculated relative stabilities of the phosphorus and arsenic hydrides. Since the s–p gap is greater in As than in P, any structure that leaves an s-type lone pair intact would be more preferred by As than P. Therefore, AsH_3 and AsH_4^- have greater stabilities than their phosphorus counterparts. This rationalizes most of the trends in Tables III and V.

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Table VIII. Highest Occupied Molecular Orbital (HOMO) Levels, in eV

	PH_n	AsH_n	PCl_n
AX_3	−10.38	−10.16	−11.63 (−11.21)[a]
AX_4^+	−22.78	−21.68	−19.17
AX_4^-	−1.27	1.56	−5.78
AX_5	−8.84	−8.58	−12.66
AX_6^-	−2.98	−3.17	−8.02

[a] With d functions on chlorine.

of eigenvalues for all species studied here are available upon request. They show an expected upward shift of the levels from PH_n to AsH_n, except for the HOMO levels of AsH_4^- and AsH_6^-. Nevertheless, this shift is small. We give in Table VIII the HOMO levels, which can be related to the first ionization potentials through Koopmans' theorem.

From a structural point of view, an ion such as PCl_5^{2-} (which is not known, but SbF_5^{2-} and $SbCl_5^{2-}$ are known) can be related to PCl_6^- since both have 6 electron pairs around the phosphorus atom. Consequently one can predict for PCl_5^{2-} a C_{4v} structure with an angle $\angle(r_{\mathrm{basal}},r_{\mathrm{apical}}) < 90°$. The situation of PCl_6^{3-} is different[58] since this ion possesses a seventh lone pair that may or may not be stereochemically active, giving a fluxional, near-octahedron like XeF_6 or a rigid octahedron like $TeCl_6^{2-}$.

In conclusion, the main results of our calculations are the following: (1) pentacoordinate phosphorus and arsenic compounds have a Lewis acid character; (2) hexacoordinate PX_6^- species have a rigid structure,[59] unlike PX_5 species; (3) their isomerization occurs preferably through bond rupture via a pentacoordinate intermediate; (4) structures of phosphorus and arsenic compounds are similar and so are the barriers to pseudorotation in PH_5 and AsH_5; and (5) some energetic differences between phosphorus and arsenic multicoordinate compounds are significant, for instance the tendency toward a greater stability for arsoranides.

Acknowledgment. We are indebted to Drs. A. Klaebe, M. Koenig, and J. G. Wolf for many discussions and comments and to the referees for helpful criticisms.

Registry No. PH_3, 7803-51-2; AsH_3, 7784-42-1; PCl_3, 7719-12-2; PH_4^+, 16749-13-6; AsH_4^+, 53250-40-1; PCl_4^+, 15169-50-3; PH_4^-, 20774-06-5; AsH_4^-, 90858-36-9; PCl_4^-, 29962-22-9; PH_5, 13769-19-2; AsH_5, 16612-59-2; PCl_5, 10026-13-8; PH_6^-, 79839-88-6; AsH_6^-, 90858-37-0; PCl_6^-, 16920-87-9; P, 7723-14-0; As, 7440-38-2; H^+, 12408-02-5; H^-, 12184-88-2; H_2, 1333-74-0; Cl_2, 7782-50-5; Cl^-, 16887-00-6.

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(57) In PH_3 and AsH_3, we have the ratio $(k_{PH}/k_{AsH})^{1/2} = 1.09$ which is, incidentally, the ratio of the corresponding stretching frequencies (McKean, D. C.; Torio, I.; Morrisson, A. R. *J. Phys. Chem.* **1982**, *86*, 307), but the latter may follow directly from the atomic masses involved.

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(59) At least when X = H or Cl. Recently, fluxional PX_6^- species containing three or more fluorine atoms have been reported: Dillon, K. B.; Platt, A. W. G. *J. Chem. Soc., Chem. Commun.* **1983**, *19*, 1089.

Deoxygenation of a Cluster-Coordinated Nitric Oxide

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Abstract: The reaction of $[Fe(CO)_3(NO)]^-$ with $Ru_3(CO)_{12}$ yields the nitrosyl carbonyl cluster $[FeRu_3(CO)_{12}(NO)]^-$. The rate of this reaction shows a first-order dependence on the concentration of $Ru_3(CO)_{12}$ and is inhibited by addition of excess CO. A single-crystal X-ray crystallographic analysis of $PPN[FeRu_3(CO)_{12}(NO)]$ [$P2_1/c$ space group, a = 19.690 (4) Å, b = 16.262 (3) Å, c = 15.911 (5) Å, β = 107.24 (2)°, Z = 4] revealed that the $FeRu_3$ tetrahedral core contained a terminal, linear nitrosyl ligand bound to the iron. Three carbonyls bridge the three iron–ruthenium bonds such that the overall symmetry is C_3. $[FeRu_3(CO)_{12}(NO)]^-$ cleanly reacts to form CO_2 and the nitrido cluster $[FeRu_3N(CO)_{12}]^-$. A structural analysis of the Et_4N^+ salt of this cluster [$P\bar{1}$] space group, a = 12.464 (1) Å, b = 12.697 (1) Å, c = 9.437 (2) Å, α = 94.40 (2)°, β = 100.17 (2)°, γ = 107.75 (1)°, Z = 2] revealed that it has a butterfly framework of metal atoms with the nitrogen coordinated to all four metals. Three terminal carbonyl ligands are also coordinated to each metal. The iron is disordered over all four sites in the structure which means that two isomeric forms exist and cocrystallize. Isomer I contains Fe in the wing-tip position while the other (II) contains Fe in the hinge position. Solution spectroscopic evidence (infrared, ^{13}C NMR and ^{15}N NMR) shows that both isomers persist in solution. Measurement of the equilibrium constant for the isomerization, I $\rightleftarrows$ II, at several temperatures between 25 and 68 °C yielded $\Delta H = -3.5 + 1.0$ kcal/mol and $\Delta S = -13 \pm 2$ eu. The rate of conversion of I $\rightarrow$ II at 25 °C is $(4.2 \pm 0.2) \times 10^{-7}\ s^{-1}$. Possible mechanisms for this unique isomerization are presented. A kinetic analysis of the deoxygenation of $[FeRu_3(CO)_{12}(NO)]^-$ to give $[FeRu_3N(CO)_{12}]^-$ over the temperature range from 25 to 65 °C revealed that the deoxygenation is first order in cluster concentration. Possible mechanisms of the NO deoxygenation consistent with this and other observations are discussed.

The formation of polynuclear compounds containing main-group interstitial atoms is often a poorly understood process. With some notable exceptions[2,3] the formation of clusters with interstitial atoms also involves changes in the nuclearity of the product. Despite having a reaction that proceeds in high yield, there are often too many bonds being broken and formed to develop a clear understanding of the reaction mechanism. Reaction 1, which is an excellent synthetic reaction, exemplifies the problems faced in such a study.[4] The CO bond cleavage step (the point of exceptional interest) is just one of many involved in product formation.

$$Fe(CO)_5 + Fe(CO)_4^{2-} \rightarrow [Fe_6C(CO)_{16}]^{2-} \qquad (1)$$

Like the source of carbon in many carbido clusters[5] the source of nitrogen in nitrido clusters is derived from its monoxide.[6-13]

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[1] Fellow of the Alfred P. Sloan Foundation (1983–1985).

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