

# Theoretical Study on the Structures of Iminopnictoranes and Their Reactions with Formaldehyde

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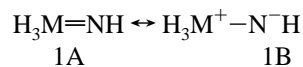
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The geometries and energies of the iminopnictoranes ( $H_3M=NH$ ;  $M = P, As, Sb, \text{ and } Bi$ ) and their reaction paths with formaldehyde are predicted by means of ab initio calculations. The multiplicity of  $M=N$  bonds is discussed by comparing the  $M=N$  and  $M-H$  bond lengths, the bond length ratios  $M=N:M-N$ , the bond angles of  $M-N-H$ , and the barrier to internal rotation about the  $M=N$  bond with those of the ylides, and it was concluded that the contribution of the ionic canonical form  $M^+-N^-$  is much more important than that of the  $M=N$  form. For the two reaction routes of the iminopnictoranes with formaldehyde (aza-Wittig and Corey–Chaykovsky-type reactions), all of the stationary points and transition states were fully optimized by using an analytical gradient with the LANL1DZ and the 9s5p-d/[3s2p-d] basis set (DZ-d) at the MP2 level. For  $M = P$  and  $As$ , the aza-Wittig reaction is more favorable than the Corey–Chaykovsky-type reaction from both the thermodynamic and the kinetic viewpoint. In the case of  $M = Sb$  and  $Bi$ , the Corey–Chaykovsky-type reaction takes place predominantly. The higher level calculations, such as MP4(SDTQ)/DZ-d//MP2/DZ-d and QCISD(T)/DZ-d//MP2/DZ-d, were performed to get accurate energies of these intermediates and transition states.

## Introduction

There is considerable interest in the structures and reactions of iminopnictoranes because of their similarity with methylenepnictogens (ylides). Iminopnictoranes are represented as resonance hybrids of the two canonical structures 1A and 1B, simple analogues to ylides.



There must be some differences between them in their reactivities and electron densities, as well as in the multiple bonding properties between the nitrogen and the pnictogen's  $M$ , depending on the degree of negative hyperconjugation from the nitrogen lone pair orbital to the  $\sigma^*$  orbital of  $M-H$  bonds ( $n-\sigma^*$ )<sup>1</sup> or on the overlap between the filled nitrogen 2p-orbital and the vacant d-orbitals on the  $M$  atoms ( $p\pi-d\pi$ ). While the latter is a classical idea about the double bond character of the hypervalent compounds, the  $\pi_Y-\sigma_{AX}^*$  negative hyperconjugation has been recently used to rationalize the bonding in various hypervalent  $X_3AY$  species, such as  $H_3PO$  and  $H_3PN^-$ ,<sup>1</sup> which are isoelectronic to  $H_3P=NH$  as well as to  $H_3P=CH_2$ . In this paper, while the MN single bonds in the reference aminopnictogens,  $H_2M-NH_2$ , are referred to as  $M-N$ , the MN bonds in iminopnictoranes are mentioned as  $M=N$ , irrespective of the degrees of their double bond characters.

Iminopnictoranes and methylenepnictogens are isoelectronic and undergo a series of interesting chemical reactions that have been utilized extensively in synthetic works. Iminophosphoranes were synthesized in 1919 by Staudinger and Meyer<sup>2</sup> and

were proved to have versatile properties. Mann and Chaplin prepared *N-p*-toluenesulfonyliminotriphenylphosphorane by the reaction of triphenylphosphine with chloramine-T.<sup>3</sup> Recently, other methods have been developed, such as the Krisanov reaction<sup>4</sup> and the reaction of ylides with Schiff's base.<sup>5</sup> Iminoarsorane is isoelectronic with arsonium ylides. However, the chemistry about iminoarsorane is less known than that of arsonium ylides. The only known example of an iminoarsorane is iminotriphenylarsorane, which was prepared by treatment of triphenylarsine with chloramine.<sup>6</sup> Little is known about iminostiboranes. Wittig and Hellwinkel reported the synthesis of triphenylstibonium *N*-tosylimine by the reaction of triphenylstibine with chloramine-T.<sup>7</sup> There is no report about the existence of an iminobismorane so far. Concerning their molecular structure, X-ray crystallography,<sup>8</sup> <sup>13</sup>C-NMR,<sup>8–10</sup> <sup>31</sup>P-NMR,<sup>9–13</sup> PE,<sup>14</sup> and IR spectra,<sup>15,16</sup> and the dipole moments<sup>17</sup> of substituted iminophosphoranes have been reported.

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Since the use of iminophosphorane as a versatile reagent was reported in 1970, many research papers and reviews<sup>18–21</sup> have been written in great detail about the various uses in organic synthesis from the synthetic viewpoints. As aza-ylides, iminopnictoranes are able to react with both nitrogen and pnictogen. They are readily protonated to give the corresponding aminophosphonium salts in the presence of mineral acids<sup>22–24</sup> and are prone to hydrolysis, giving amine and pnictogen oxides.<sup>25,26</sup> Alkylations,<sup>22,27,28</sup> acylations,<sup>29</sup> and halogenations<sup>24,30</sup> are also well-known reactions of iminophosphoranes. Besides these reactions, analogous to methylenepnictogens (ylides), iminopnictoranes can react under mild and neutral conditions with carbonyl compounds, an excellent method to introduce C=N double bonds in an aza-Wittig reaction. Especially, the intramolecular aza-Wittig reaction has played an important role in the synthesis of nitrogen-containing heterocycles. The mechanism of aza-Wittig reactions did not attract much attention because it was supposed to be very similar to that of the isoelectronic Wittig reaction. It was simply mentioned that the first step of the aza-Wittig reaction should be betaine formation via nucleophilic attack of the nitrogen on the carbonyl carbon, followed by the transfer of oxygen from carbon to phosphorus, and that the reaction could be either reversible or irreversible.<sup>31</sup> On the other hand, there are many experimental and theoretical reports about the mechanism of the Wittig reaction.<sup>32–41</sup> The theoretical studies on the Wittig reaction revealed the direct formation of four-membered intermediates by a concerted (2s + 2s) mechanism and the absence of a betaine in a gas phase. To our knowledge, no theoretical study on the aza-Wittig reaction has been carried out so far. There is no experimental report about the Corey–Chaykovsky-type reaction products from the reaction of iminopnictoranes with carbonyl compounds so far; in this reaction, a trivalent pnictogen molecule would act as a leaving group.

In order to get quantitative information about the molecular structure, the relative energetics of iminopnictoranes (H<sub>3</sub>M=NH; M = P, As, Sb, and Bi), and about the reaction path in aza-Wittig and Corey–Chaykovsky-type reactions, we have performed ab initio calculations on iminopnictoranes and on the simple model aza-Wittig reaction



and the Corey–Chaykovsky-type reaction



The simplest models for iminopnictoranes and carbonyl compounds were chosen, replacing all of the substituents on the heavy atoms by hydrogen atoms. Although none of these model compounds, except formaldehyde, is known experimentally, it can be assumed that the intrinsic property of the real compounds and that of the reaction behavior is present in these model compounds. The validity of this hypothesis would be verified by studying the substituent effect on the structures and energetics. Also, it is reasonable to expect, because of their isoelectronic structure with ylides, that Corey–Chaykovsky-type reactions for iminopnictoranes take place. The ab initio calculations<sup>32</sup> at the MP2/DZ-d level about the corresponding reactions of ylides with formaldehyde have been recently reported, and some comparisons will be made with the present results.

### Method of Calculations

The first basis set used with the LANL1DZ basis set that was stored in the Gaussian program, which is composed from D95V for first-row atoms<sup>42</sup> and the Los Alamos effective core potentials (ECP) plus the valence double zeta (DZ) basis functions, developed by Wadt and Hay,<sup>43</sup> for pnictogens. In the second basis set, abbreviated as DZ-d, the LANL1DZ basis set was modified by adding a set of five d-type polarization functions for the heavy atoms (d exponents: 0.600 (C), 0.864 (N), 1.154 (O), 0.340 (P), 0.293 (As), 0.211 (Sb), and 0.185 (Bi)).

The structures of all of the reactants, products, intermediates, and transition states were optimized by using the analytical gradient methods of Gaussian92<sup>44</sup> at the second-order Moller–Plesset perturbation (MP2) level<sup>45</sup> with the DZ-d basis set. The optimizations were performed without any constraints, i.e., all of the 3N-6 internal coordinates were relaxed. Vibrational analysis was carried out at the MP2 level to characterize all of the stationary points. Furthermore, the vibrational frequencies thus calculated, without scaling, were utilized to calculate the zero-point correction.

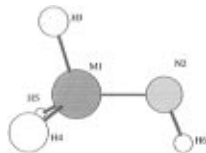
In order to get more reliable energetics beyond the MP2 level perturbation, the energy calculations on the MP2 optimized structures were performed with full fourth-order Moller–Plesset perturbations (MP4(SDTQ)) and quadratic configuration interaction, including single and double substitutions with triples contribution (QCISD(T)). Throughout the paper, for clarity, we used the standard notation to specify the level of calculation and the structure used. For instance, MP4(SDTQ)/DZ-d/MP2/DZ-d designates and MP4(SDTQ) calculation with the DZ-d basis set using the structure determined at the MP2 level with the same basis set.

### Results

**Character of Iminopnictoranes.** The geometrical data of all of the iminopnictoranes (H<sub>3</sub>M=NH; M = P, As, Sb, and Bi) are listed in Table 1 along with the M–N bond lengths for H<sub>2</sub>M–NH<sub>2</sub> at the MP2/DZ-d level of calculations. The relevant geometrical data of ylides (H<sub>3</sub>M=CH<sub>2</sub>) at the MP2/DZ-d level are cited in Table 2. Tables 1 and 2 contain the bond length

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**Table 1.** Calculated Parameters<sup>a</sup> of H<sub>3</sub>M=NH (M = P, As, Sb, and Bi)

M	M=N	BO <sup>b</sup>	M-H3	M-H4,5	N-H	M-N-H	H <sub>3</sub> MNH	M <sup>c</sup>	N <sup>d</sup>	M=N:M-N <sup>e</sup> (M-N <sup>f</sup> )
P	1.601	1.667	1.414	1.438	1.022	113.6	180.0	1.063	-1.299	0.912 (1.755)
As	1.715	1.537	1.504	1.533	1.023	111.3	180.0	1.456	-1.388	0.919 (1.866)
Sb	1.899	1.492	1.687	1.720	1.030	111.4	180.0	1.791	-1.431	0.927 (2.049)
Bi	1.977	1.315	1.738	1.776	1.036	107.4	180.0	1.630	-1.301	0.927 (2.133)

<sup>a</sup> At MP2/DZ-d level. All lengths in angstroms and angles in degrees. <sup>b</sup> Meyer-Mulliken NBO bond order of H<sub>3</sub>M-NH at MP2/DZ-d. <sup>c</sup> Natural charges on M. <sup>d</sup> Natural charges on N. <sup>e</sup> Bond lengths ratio. <sup>f</sup> Bond lengths of H<sub>2</sub>M-NH<sub>2</sub>.

**Table 2.** Calculated Parameters<sup>a</sup> of H<sub>3</sub>M=CH<sub>2</sub> (M = P, As, Sb, and Bi)

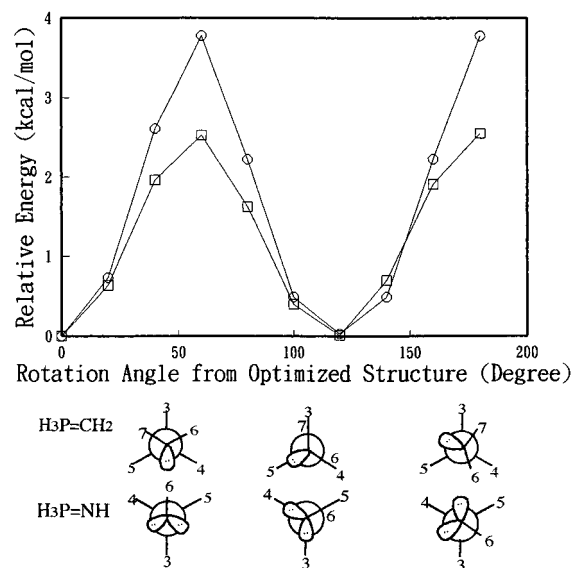
M	M=C	BO <sup>b</sup>	M-H3	M-H4,5	C-H	M-C-H	M <sup>c</sup>	C <sup>d</sup>	M=C/M-C <sup>e</sup> (M-C <sup>f</sup> )
P	1.679	1.414	1.453	1.417	1.094	114.1	0.889	-1.167	0.902 (1.861)
As	1.799	1.301	1.557	1.508	1.098	111.5	1.056	-1.182	0.905 (1.988)
Sb	1.933	1.271	1.740	1.693	1.102	110.2	1.403	-1.233	0.915 (2.113)
Bi	2.124	1.049	1.779	1.746	1.109	105.3	1.264	-1.108	0.943 (2.252)

<sup>a</sup> At MP2/DZ-d level. <sup>b</sup> Meyer-Mulliken NBO bond order. <sup>c</sup> Natural charges on M. <sup>d</sup> Natural charges on C. <sup>e</sup> Bond length ratio. <sup>f</sup> Bond length of H<sub>2</sub>M-CH<sub>3</sub>.

ratio (M=N:M-N) of the iminopnictoranes to the aminopnictogens (H<sub>2</sub>M-NH<sub>2</sub>) and that (M=C/M-C) of the ylides to the methylpnictogens (H<sub>2</sub>M-CH<sub>3</sub>). The X-ray crystallography for *N*-pyrid-4-yl-iminotriphenylphosphorane (Ph<sub>3</sub>PNPy) revealed the P=N bond length to be 1.574 Å<sup>46</sup> and that for phenyliminotriaminophosphorane to be 1.539 Å.<sup>47</sup> Although the P=N bond distance calculated at the MP2/DZ-d level seems to be inconsistent with the X-ray analysis, this discrepancy could be ascribed to the substituent effects. The RHF/4-31G\* calculation has, on the other hand, given the bond length to be 1.532 Å,<sup>48</sup> closer to the experimental ones. However, as shown later, the restricted Hartree-Fock (RHF) wave function is not satisfied to give the proper geometry and energetics. Accordingly, we keep using the results obtained at correlated level.

The M-N-H bond angles are close to the tetrahedral angle (109.5°), suggesting that the nitrogen atoms in all of the compounds calculated have essentially sp<sup>3</sup> hybridization and that they have two lone pairs opposite of one of the M-H bonds. Note that there is a slight variation in the bond angles; the M-N-H bond angles change in the order of P (113.6°) > As (111.3°) = Sb (111.4°) > Bi (107.4°). Since there is no significant difference in the bonding nature among pnictogens, the change in the M=N bond lengths, which become longer progressively from 1.601 Å for M=P to 1.977 Å for M=Bi, simply reflects the change in the size of M.

One way to estimate the contribution of the double bond character in M=N bonds based on these bond lengths might be with the bond length ratio (M=N:M-N shown in Table 1). The ratio listed in Table 1 varies from 0.912 for P=N to 0.927 for Sb=N and Bi=N; comparing this with the M-N bonds, the M=N bonds are substantially shorter, suggesting the existence of the double bond character. Note that the electrostatic attraction force in the canonical form, M<sup>+</sup>-N<sup>-</sup> (vide infra), would give shorter distances than those of the single bond, and therefore, the bond length ratio could exaggerate the double bond character. It is worth mentioning that for all of the iminopnictoranes, the M-H4,5 bonds situated anti-periplanar to the lone

**Figure 1.** Rotation barrier about P=N and P=C bonds at the MP2/DZ-d level: (○), H<sub>3</sub>P=CH<sub>2</sub>; (□), H<sub>3</sub>P=NH.

pairs are longer than the M-H3 bond anti-periplanar to N-H bond, suggesting the existence of the n-σ\* negative hyperconjugation.

Because of their smaller electronegativity, the negative hyperconjugation in the iminopnictoranes with a heavier M is harder to take place, resulting in the smaller double bond character, which can be seen in various results in addition to the bond length ratio. The M-N-H angles decrease from P to Bi, which would be increased by the n-σ\* negative hyperconjugation. The Mayer-Mulliken bond orders shown in Table 1 also decrease from 1.667 for M = P to 1.315 for M = Bi.

The rotational barriers to the internal rotation around M=N bonds could be the energetic measure of the double bond character. The energy profile of the rotation about the P=N bond of the model iminophosphorane as a function of the HPNH dihedral angle at MP2/DZ-d level is shown in Figure 1. The geometries were optimized with the HPNH dihedral angle fixed at 20°. The small energy barrier of 2.54 kcal/mol was obtained. The rotational barrier around the P=N bond of 2.13 kcal/mol

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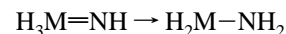
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for iminophosphorane was reported by others with ab initio calculations at the RHF/6-31G\* level<sup>49</sup> and that of 1.67 kcal/mol for Me<sub>3</sub>PPh with the CNDO/2 method.<sup>50</sup> These small barriers show that the negative hyperconjugation would not energetically make a significant contribution to the barrier to the internal rotation. The  $\pi\text{p}-\text{d}\pi$  interaction might diminish the barrier, which is invariant to the rotational angle.

The above structural features suggest that  $n-\sigma^*$  negative hyperconjugation exists in iminopnictoranes. However, the positive charges on the M atoms of iminopnictoranes are not counterbalanced by the  $n-\sigma^*$  hyperconjugation (Table 1), and there are large negative charges on the nitrogen atoms of iminopnictoranes, demonstrating that the contribution of an ionic canonical form  $\text{M}^+-\text{N}^-$  is much more important than  $\text{M}=\text{N}$ . Consistent with the negative charges, the <sup>31</sup>P-NMR chemical shifts of *N*-phenyltriarylphosphorane fell in the range of  $-5$  to  $+8$  ppm, relative to 85% H<sub>3</sub>PO<sub>4</sub>, and are deshielded by ca. 30 ppm from their phosphonium salts.<sup>9-14</sup> The <sup>15</sup>N-NMR chemical shifts of the iminophosphoranes were found to be very shielded compared with those of the amines<sup>51</sup> and deshielded compared with the other  $\text{M}=\text{N}$  compounds.<sup>52</sup> Also, the lone pair basicity of the nitrogen atom on the iminophosphorane was investigated by using IR spectroscopy<sup>53</sup> and was found to be stronger than those of aminophosphines (R<sub>2</sub>PNR'<sub>2</sub>).

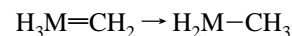
Next, the above geometrical and electronic features for iminopnictoranes are compared with those for ylides briefly. As shown in Table 2, the M-H<sub>3</sub> bond anti to the lone pair of any of the ylides is longer than the M-H<sub>4,5</sub> bonds anti to the C-H bonds, suggesting  $n-\sigma^*$  hyperconjugation. The trend in the bond length ratio  $\text{M}=\text{C}:\text{M}-\text{C}$  (P (0.902) < As (0.902) < Sb (0.915) < Bi (0.943)) is similar to that for iminopnictoranes. Comparison with  $\text{M}=\text{N}:\text{M}-\text{N}$  shows that for P, As, and Sb, the  $\text{M}=\text{N}$  bonds have a multiplicity smaller than that of the  $\text{M}=\text{C}$  bonds whereas the multiplicity of the  $\text{Bi}=\text{N}$  bond is larger than that of the  $\text{Bi}=\text{C}$  bond. Since the donation from the nitrogen lone pair is more difficult than that from the carbon lone pair, the trend for P, As, and Sb seems reasonable; the natural charges on the nitrogen atoms of the iminopnictoranes are much more negative than those on the carbons of the ylides. The small ratio of the Bi iminopnictorane may be ascribed to the electrostatic attraction, due to an ionic canonical structure in  $\text{Bi}=\text{N}$  bond, because of the large difference in electronegativity. The energy profile of the rotation about the  $\text{P}=\text{C}$  bond (H<sub>3</sub>P=CH<sub>2</sub>) as a function of the HPCH dihedral angle at the MP2/DZ-d level is also shown in Figure 1. The energy barrier of 3.8 kcal/mol is higher than that of 2.54 kcal/mol for iminopnictorane, consistent with the larger double bond character in the ylide. The Mayer-Mulliken bond orders of  $\text{M}=\text{C}$  bonds are much lower than those of the ylides, contrary to what was described above, suggesting that quantitative comparison of the bond character with the population analysis is difficult, as found in many other studies.

The relative stability of the iminopnictoranes can be estimated by comparing the internal transfer energies<sup>32,54-56</sup>



$$\Delta E \text{ (kcal/mol)} = -34.4 \text{ (P)}, -49.1 \text{ (As)}, \\ -63.5 \text{ (Sb)}, -63.8 \text{ (Bi)}$$

The same relative energies of ylides at the same level of calculations were reported by Naito et al.<sup>32</sup> as shown below.



$$\Delta E \text{ (kcal/mol)} = -52.3 \text{ (P)}, -68.2 \text{ (As)}, \\ -77.3 \text{ (Sb)}, -93.0 \text{ (Bi)}$$

Note that we must take the energy barrier of the H transfer into consideration to get the relative kinetic stability. Simply from these results, iminopnictoranes are thermodynamically more stable than ylides with respect to hydrogen transfer, because the energy differences between the hypervalent compounds (iminopnictoranes) and the normal valent compounds (aminopnictogens) are smaller compared with those for the corresponding ylides. Iminopnictorane, as well as ylide, with a heavier M is relatively unstable, and thus, the hydrogen transfer reaction is more exothermic than that for a lighter M; the relative stability order is  $\text{P} > \text{As} > \text{Sb} \sim \text{Bi}$ . As will be discussed in the next section, this affects the potential energy surface for the aza-Wittig and the Corey-Chaykovsky-type reaction. It is very interesting that the same level of stability for  $\text{Bi}=\text{N}$  and  $\text{Sb}=\text{N}$  can be expected. Although, as we mentioned in the Introduction, there is no report about the synthesis of any  $\text{Bi}=\text{N}$  compounds, preparing this type of compound by the same method as the preparation of  $\text{Sb}=\text{N}$  complexes might be possible.

**Aza-Wittig and Corey-Chaykovsky-type Reactions.** The model reactions of iminopnictoranes with formaldehyde are expected to proceed through the following two paths. One is the aza-Wittig reaction (1) and the other is the Corey-Chaykovsky-type reaction (2), as mentioned in the Introduction. As discussed in the last section, iminopnictoranes are largely polarized with a positive charge on the pnictogen, M, and a negative charge on the nitrogen, similar to an ylide. Thus, in reactions 1 and 2, formaldehyde carbon with a positive charge would attack nitrogen. Also, formaldehyde oxygen with a negative charge could interact with pnictogen. The previous theoretical studies have shown that although the Wittig reaction is formally a symmetry-forbidden ( $2s+2s$ ) addition, polar characters of the reagents make the reaction rather easy.<sup>32</sup>

We have determined the structures at the MP2/DZ-d level and carried out the energy calculations at the several levels as mention in Methods of Calculations section. In this section, we will use, in the discussion of the chemistry, the energies calculated at the most sophisticated level, QCISD(T)/DZ-d. The effect of electron correlation will be discussed later. The optimized structures at the MP2/DZ-d level are shown in Table 3, and the potential energy profiles, as well as the energy profiles with zero-point corrections, are shown in Figures 2, 3, 4, and 5 for P, As, Sb, and Bi, respectively.

**Aza-Wittig Reaction.** We found there are the three intermediates, I1, I2, and I3, and three transition states, T1, T2, and T3, for aza-Wittig reactions of any pnictogen, M. The first intermediate (I1) has long N-C and M-O distances, and as a

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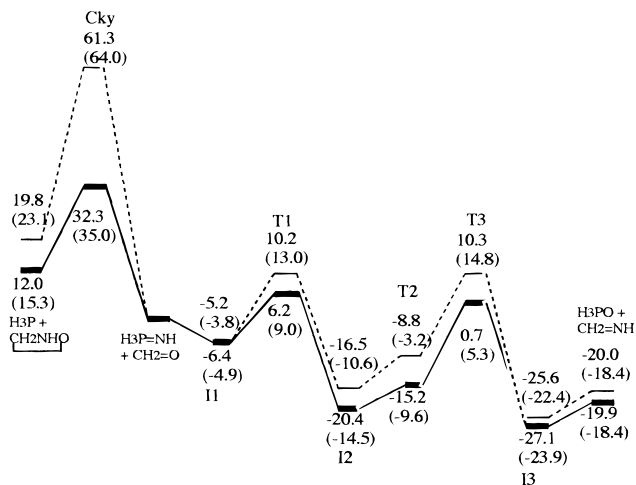
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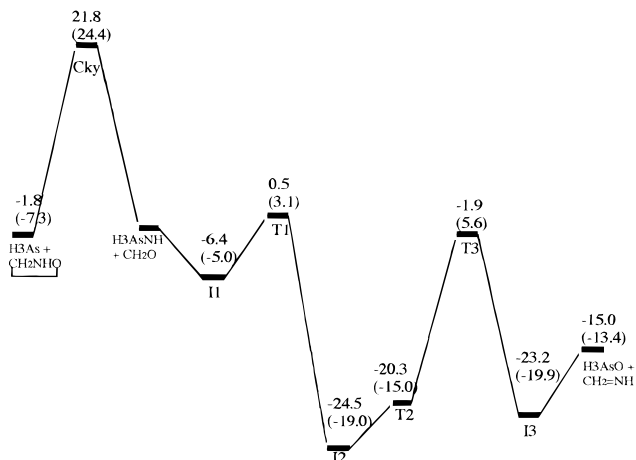
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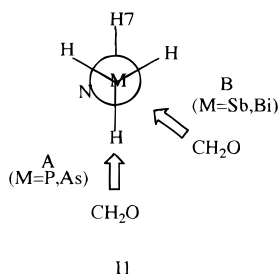


**Figure 2.** Energy profile for reaction of  $\text{H}_3\text{P}=\text{NH}$  with  $\text{H}_2\text{CO}$ , calculated at the RHF/DZ-d/MP2/DZ-d (dotted line) and QCISD(T)/DZ-d/MP2/DZ-d (solid line) levels. Energies (kcal/mol) are relative to the reactants, and the energies in parentheses are the values with the zero-point correction.

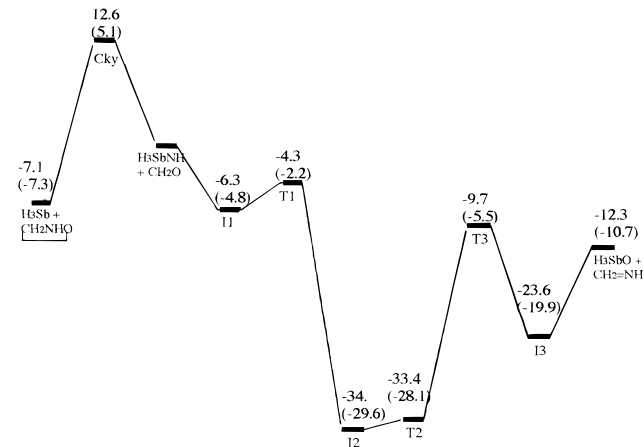


**Figure 3.** Energy profile for reaction of  $\text{AsH}_3=\text{NH}$  with  $\text{H}_2\text{CO}$ , calculated at QCISD(T)/DZ-d/MP2/DZ-d (solid line) level. Energies (kcal/mol) are relative to the reactants, and the energies in parentheses are the value with the zero-point correction.

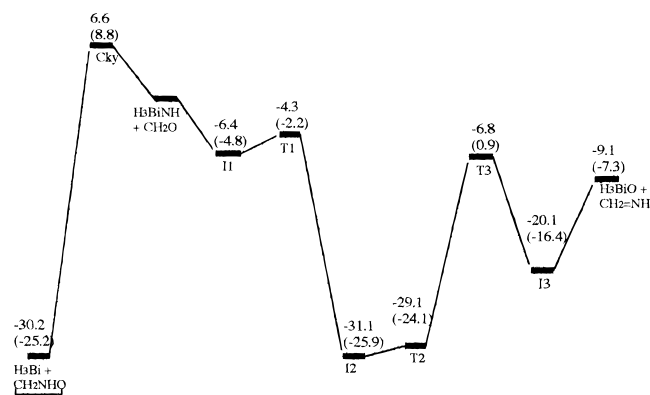
result, each fragment has only a small perturbation from the geometry of the isolated reactant, suggesting that the dipole-dipole interaction between reactants is a driving force of complexation. Consistent with this, the formaldehyde-iminopnictorane binding energy is not very large, 5 kcal/mol for any M. While for every M I1 has an almost planar four-membered ring, there is difference in the location of H7; H7 for P and As is almost in the ONMC plane, but H7 for heavier Sb and Bi is out of the plane, with the ONMC dihedral angle of about  $53^\circ$ . This difference can be understood as follows. There are two sides available in the complexation of formaldehyde to iminopnictoranes, as shown in the scheme below, depending on M.



11



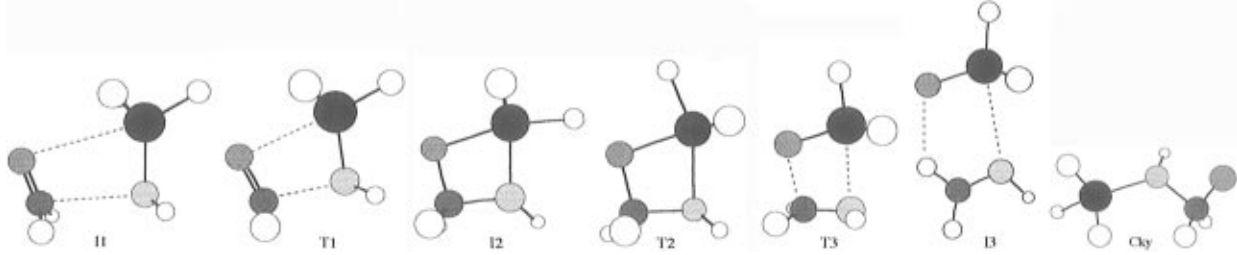
**Figure 4.** Energy profile for reaction of  $\text{H}_3\text{Sb}=\text{NH}$  with  $\text{H}_2\text{CO}$ , calculated at QCISD(T)/DZ-d/MP2/DZ-d level. Energies (kcal/mol) are relative to the reactants, and the energies in parentheses are the values with the zero-point correction.



**Figure 5.** Energy profile for reaction of  $\text{H}_3\text{Bi}=\text{NH}$  with  $\text{H}_2\text{CO}$ , calculated at QCISD(T)/DZ-d/MP2/DZ-d level. Energies (kcal/mol) are relative to the reactants, and the energies in parentheses are the values with the zero-point correction.

When formaldehyde complexes from side A, as seen for  $\text{M} = \text{P}$  and  $\text{As}$ , the formaldehyde carbon with a positive charge can interact with the two lone pair orbitals on the nitrogen simultaneously and, thus, strongly. However, one of the  $\text{M}-\text{H}$  bonds would prohibit the formaldehyde oxygen from approaching the pnictogen,  $\text{M}$ . As a matter of fact, the  $\text{M}-\text{O}$  distances of I1 for  $\text{M} = \text{P}$  and  $\text{As}$  (3.394 and 3.469 Å) are even longer than those for  $\text{M} = \text{Sb}$  and  $\text{Bi}$ , although the size of the  $\text{P}$  and  $\text{As}$  atoms is smaller. While for  $\text{M} = \text{P}$  and  $\text{As}$  the  $\text{C}-\text{N}$  interaction occurs predominantly in this manner, the formaldehyde oxygen interacts strongly with heavier  $\text{Sb}$  and  $\text{Bi}$ , because these atoms have larger positive charges (Table 1). As a result, the  $\text{M}-\text{O}$  distances for  $\text{M} = \text{Sb}$  and  $\text{Bi}$  are shorter than those for  $\text{M} = \text{P}$  and  $\text{As}$  and, accordingly, side B is chosen to avoid steric hindrance and to favor  $\text{M}-\text{O}$  interaction. The strong  $\text{M}-\text{O}$  interaction compensates for the loss of interaction of the formaldehyde carbon with one of the nitrogen lone pair orbitals.

The first transition state (T1) leads to formation of the second cyclic intermediate (I2). Thus, at T1, formaldehyde approaches iminopnictorane resulting in the formation of the almost planar, tight OMNC ring. The newly forming  $\text{N}-\text{C}$  bond for  $\text{M} = \text{P}$  is shorter than that for  $\text{M} = \text{As}$ , which, in turn, is shorter than that for  $\text{M} = \text{Sb}$  and  $\text{Bi}$ . The  $\text{C}-\text{O}$  bond, which is changed from a double bond to a single bond, is the longest for  $\text{M} = \text{P}$ , those for  $\text{M} = \text{Sb}$  and  $\text{Bi}$  are the shortest, and that for  $\text{M} = \text{As}$  is in between. These structural features indicate that T1 for  $\text{M} = \text{P}$  is located later, for  $\text{M} = \text{As}$  next, and for  $\text{M} = \text{Sb}$  and  $\text{Bi}$  earlier, consistent with the order of energy of reaction,  $\text{I1} \rightarrow$

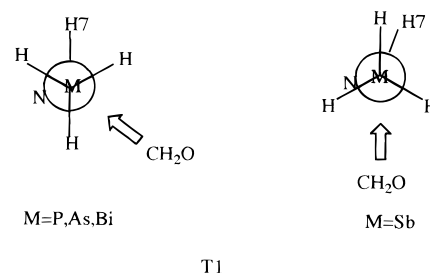
**Table 3.** Optimized Geometries<sup>a</sup> of the Intermediates and Transition States of the Reaction of Iminopnictoranes with Formaldehyde


M	M-N	N-C	C-O	M-O	O-M-N	M-N-C	N-C-O	C-O-M	OMNC	OMNH7
II										
P	1.606	2.698	1.229	3.394	70.1	103.6	103.9	82.2	1.7	184.9
As	1.720	2.703	1.229	3.469	67.6	104.5	104.3	83.5	0.8	181.3
Sb	1.909	2.697	1.230	3.300	71.9	95.4	105.9	86.5	2.3	233.5
Bi	1.992	2.624	1.232	3.182	71.4	94.0	104.7	89.6	2.4	233.4
T1										
P	1.647	1.856	1.275	2.510	70.2	100.4	104.0	84.0	6.6	214.9
As	1.751	2.015	1.261	2.577	71.3	97.2	103.3	88.0	2.3	220.8
Sb	1.925	2.186	1.247	2.671	68.5	96.9	97.7	96.9	0.0	185.0
Bi	2.006	2.176	1.249	2.751	67.2	96.3	100.9	94.9	4.1	210.1
I2										
P	1.724	1.480	1.409	1.830	74.6	94.9	96.5	93.0	6.8	216.2
As	1.845	1.486	1.409	1.929	71.6	94.5	99.4	93.5	6.5	223.6
Sb	1.995	1.477	1.413	2.070	66.4	97.0	100.8	95.8	0.0	179.9
Bi	2.142	1.491	1.415	2.143	65.5	93.1	105.9	95.3	2.6	240.0
T2										
P	1.844	1.459	1.447	1.727	75.2	90.6	97.3	75.2	7.2	234.0
As	1.941	1.466	1.441	1.851	71.9	91.2	100.0	95.8	6.7	235.1
Sb	2.092	1.473	1.435	2.023	67.2	92.4	103.1	96.5	5.8	234.2
Bi	2.179	1.481	1.426	2.115	65.2	92.0	105.5	96.3	6.2	237.9
T3										
P	2.289	1.347	1.831	1.598	77.6	83.4	102.3	94.3	12.3	264.3
As	2.390	1.340	1.897	1.706	75.3	84.8	103.1	93.8	13.9	265.5
Sb	2.530	1.327	2.055	1.871	73.0	88.8	102.2	92.2	16.1	265.9
Bi	2.618	1.328	2.041	1.941	70.6	88.1	104.0	93.3	16.1	266.5
I3										
P	3.036	1.296	3.109	1.527	80.9	103.6	81.0	94.5	0.0	180.0
As	2.973	1.296	3.071	1.645	80.1	106.0	81.0	92.9	0.1	180.0
Sb	2.753	1.295	2.997	1.829	79.6	113.3	78.5	88.7	0.0	180.0
Bi	2.857	1.296	3.029	1.898	78.8	111.3	81.2	88.8	0.0	180.0
Cky										
P	1.860	1.494	1.333	2.001	122.8	89.9	203.5	71.8		
As	1.928	1.532	1.316	2.069	124.1	92.8	198.0	65.4		
Sb	2.051	1.595	1.299	2.162	126.8	96.2	195.8	58.4		
Bi	2.093	1.707	1.278	2.264	129.9	97.6	178.3	49.1		

<sup>a</sup> At MP2/DZ-d level.

I2, P (-14.0 kcal/mol) > As (-18.1) > Sb (-28.3) ~ Bi (-24.7). The activation energy relative to I1 agrees with this order as well, P (12.5 kcal/mol) > As (6.9) > Sb (2.0) ~ Bi (2.2). The transition state for the more exothermic reaction is located earlier and the corresponding activation energy is smaller, consistent with the Hammond principle. Note that the M-O bond distance is an exception. While the newly forming M-O bond distance at T1 for M = P is 1.37 times longer than that of I2, that for M = Bi is only 1.28 times longer; though T1 for M = P is located earlier, the M-O bond formation is not so. Presumably, the M-O static interaction mentioned above for the heavier M results in the acceleration of M-O bond formation.

In T1, one can again observe the difference in the position of H7 as shown below. The conformation of T1 for M = P, As, and Bi is similar to one another, where the nitrogen atom with partially formed N-C bond is pyramidalized. On the other hand, H7 for M = Sb is almost in the OMCN plane. Thus, the nitrogen atom is planar and seems to be sp<sup>2</sup> hybridized (vide infra).



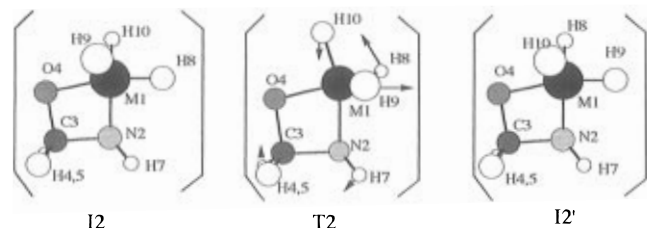
As stated above, the reaction from I1 to I2 is exothermic. The products, I2, are in a deep well on the potential energy surface. Since the order of the exothermicity is parallel to that of the stability of the iminopnictoranes discussed in the last section, the larger exothermicity for M = Sb and Bi may be ascribed to the instability of the iminopnictoranes.

The central pnictogen of I2 is five-coordinate and hypervalent. The electronegative oxygen atom in I2 is located at an apical position, and thus, I2 should be a stable conformer. Vibrational

analysis shows I2 has all positive frequencies, and thus, it is an equilibrium structure.

Since the size of the central M is different, in I2 there are differences in the bond angles, such as the M–N–C angle, among four M. However, the difference in the N–C and C–O bond lengths is small. In I2, similar to T1, H7 for M = Sb is almost in the OMNC plane. The position of H7 might be determined by the subtle balance between the nitrogen hybridization and the sterical interaction among the N–H7 bond and the adjacent C–H bond, as well as the in plane M–H bonds.

I2, having a trigonal bipyramidal M, could undergo a pseudorotation to form another four-membered cyclic T2 that has, in turn, a less electronegative nitrogen atom at an apical position and, therefore, is about 2–5 kcal/mol less stable than I2; the more electronegative substituent would favor the apical position (apicophilicity). T2 has one imaginary frequency, and the intrinsic reaction coordinate, IRC, search starting from T2 reveals that T2 is the pseudorotational transition state at the M center, leading to I2 and I2'. The structural changes during the pseudorotation connecting I2 and I2' through T2 are shown below. The arrows on T2 indicate the vectors of the imaginary frequency, the reaction coordinate vectors. The activation energy for this pseudorotation decreases in the order. P (5.2 kcal/mol) > As (4.2) > Sb (1.2) ~ Bi (2.0). Comparison of



the geometrical parameters between I2 and T2 shows the structural features of hypervalent compounds. For instance, the apical M–O bond in I2 and the apical M–N bond in T2 are longer than the equatorial M–O bond in T2 and the equatorial M–N bond in I2, respectively. In I2, the position of H7 is almost the same for every M.

In the aza-Wittig reaction, the imine finally dissociates from the cyclic intermediates. The calculations showed that this dissociation passes through T3. This process was traced by IRC analysis starting from T3. At one end of the reaction path from T3 is the hydrogen bonded product, I3, and at the other end is T2, the transition state for pseudorotation. Therefore, before reaching T2, there must be a point where the reaction coordinate bifurcates<sup>58</sup> toward I2 and I2' on the potential energy surface; i.e., in H<sub>3</sub>MO approaching H<sub>2</sub>C=NH, we have two possible products, I2 and I2', depending on the conformation of the H<sub>3</sub>M component. This also indicates that the real reaction would not necessarily pass through the transition point T2. Consequently, the energy differences between I2 and I3 and between I2 and T3 are regarded as an energy of reaction and an activation energy, respectively. The similar features of the potential energy surface were found in the theoretical calculations of Wittig reactions.<sup>32</sup>

The energy of reaction for this step, I2 → I3, increases in the order, P (–6.8 kcal/mol) < As (1.3) < Sb (10.4) ~ Bi (11.0). This order is opposite of that for the reaction I1 → I2. This is not surprising, because I2 → I3 giving H<sub>3</sub>M=O, isoelectronic to H<sub>3</sub>M=NH, is regarded as a 'reverse' reaction of I1 → I2, starting from H<sub>3</sub>M=NH. It is also suggested that the order of the relative stability for pnictogen oxides is the same as that

for iminopnictorane. The activation energy increases in the order P (21.1 kcal/mol) < As (22.6) < Sb (24.3) < Bi (24.3), consistent with the order of the energy of reaction. The structural change is consistent too, as seen in the longer N–C bond and the shorter C–O bond for M = P at T3. It has actually been calculated<sup>32</sup> that the oxygen affinity of MH<sub>3</sub> decreases in the order P > As > Sb > Bi.

The last step, imine dissociation from complex I3, is uphill and endothermic by 7.2, 8.2, 11.3, and 11.0 kcal/mol for P, As, Sb, and Bi, respectively. Slightly different from I1, the imine binding energies in I3 is larger with the heavier elements.

The energy of the overall reactions is in the order P (–19.9 kcal/mol) < As (–15.0) < Sb (–12.3) < Bi (–9.1). This energy is formally calculated to be the difference between  $E(\text{H}_3\text{M}=\text{NH}) + E(\text{H}_2\text{CO})$  and  $E(\text{H}_3\text{M}=\text{O}) + E(\text{H}_2\text{CNH})$ . The fact that the reaction for a lighter pnictogen is more exothermic suggests that a lighter pnictogen favors H<sub>3</sub>M=O, relative to H<sub>3</sub>M=NH, and the extent of preference decreases with going down the rows. The activation energy for I2 → I3 through T3 is the largest among the elementary steps of the whole aza-Wittig reaction and, therefore, controls the overall reactivity of this reaction. Accordingly, the present calculations show that the aza-Wittig reaction for P is the easiest with the lower barrier and that, going down the rows, the reaction becomes more difficult with the higher barrier.

**Corey–Chaykovsky-Type Reaction.** The geometrical parameters of the *trans*-betaine transition state (Cky) for the Corey–Chaykovsky-type reaction are also shown in Table 3. The energy profiles for the reactions are shown in Figures 2, 3, 4, and 5 as well. IRC analysis confirmed that the reaction path from Cky leads to MH<sub>3</sub> and cyclic azaoxaridine (CH<sub>2</sub>NHO) as the products and CH<sub>2</sub>O + H<sub>3</sub>M=NH as the reactants. Contrary to the case of an ylide,<sup>32</sup> the reactant complex formation was not observed before reaching Cky.

The reaction energy becomes more negative in the order of P (12.0 kcal/mol) > As (–1.8) > Sb (–7.1) > Bi (–30.2). Since this reaction is the transformation from hypervalent compounds to normal valent compounds, this order shows the same trend as that in the relative stability that was calculated as the internal proton transfer energy. Iminopnictorane with the heavier atom is relatively less stable, and therefore, the reaction is more exothermic. This difference in the energy of reaction is reflected by the activation barrier, as well as by the structures of Cky. The activation barrier decreases in the same order, P (32.3 kcal/mol) > As (21.8) > Sb (12.6) > Bi (6.6). The N–C, C–O, and N–O bond distances clearly show that Cky for a heavier atom is located earlier, consistent with the energy of reaction and, thus, the Hammond principle. The features in the energy profiles and in the structures resulted from the stability of the iminopnictoranes.

Compared with those in T1, the N–C bond lengths of Cky are much shorter. Presumably, a two-center interaction at Cky, different from four-center interaction in T1, results in these shorter distances. The N–O bond distances being much longer than the N–C bond suggests that the bond formation at Cky is asynchronous.

**Comparison of the Energy of the Aza-Wittig and Corey–Chaykovsky-type Reaction.** The energy profiles with zero-point energy correction, that are the profiles of the enthalpy at 0 K, are shown in Figures 2–5. However, qualitatively these corrections do not affect the energy relations. While the aza-Wittig reactions for all iminopnictoranes were calculated to be exothermic, the Corey–Chaykovsky-type reactions are also exothermic, except that of iminophosphorane. The activation energies for the Corey–Chaykovsky-type reaction (P > As >

Sb > Bi) is in the reverse order as those of the rate determining step of the aza-Wittig reaction (P < As < Sb < Bi). As discussed before, they are governed by the relative stability for  $H_3M=X$  (P > As > Sb > Bi). The Corey–Chaykovsky-type reaction starts from  $H_3M=NH$ , and the aza-Wittig reaction leads to  $H_3M=O$ . For  $M = P$ , the activation energy of the rate-determining step of the aza-Wittig reaction is lower than that of the Corey–Chaykovsky-type reaction. The former is also more exothermic than the Corey–Chaykovsky-type reaction. Therefore, for  $M = P$ , the aza-Wittig reaction is more favorable. For  $M = As$ , while the activation energies for both reactions are similar, the aza-Wittig reaction is more exothermic and, therefore, should be more favorable thermodynamically. In the case of  $M = Sb$ , the activation barrier for the Corey–Chaykovsky-type reaction (ca. 5 kcal/mol) is much lower than that for the aza-Wittig reaction (ca. 24 kcal/mol). Accordingly, the former is kinetically more favorable but thermodynamically slightly less favorable. On the other hand, with  $M = Bi$ , the Corey–Chaykovsky-type reaction becomes kinetically and thermodynamically more favorable than the aza-Wittig reaction. Apparently, going down the rows the Corey–Chaykovsky-type reaction becomes easier. Although the Corey–Chaykovsky-type reaction has not been reported for pnictogens, the calculations predict that for iminobismorane, if prepared, as well as iminostiborane, the Corey–Chaykovsky-type  $S_N2$  reaction would be favored.

$SbH_3$  and  $BiH_3$  could be good leaving groups because of their poor affinity to the oxygen atom, so azaoxaridine might be a final product in the case of Sb and Bi iminopnictoranes.

**Comparison with the Ylides.** For the ylides, the differences in the reactivity among the pnictogens and in the energy profiles between the Wittig and the Corey–Chaykovsky reaction were discussed based on the bond strengths of the M–C and M–O bonds,<sup>32</sup> which is closely related to the relative stabilities used in the foregoing discussions.

As we expected, the energy profiles of the reactions of iminopnictoranes with formaldehyde are qualitatively close to those of ylides,<sup>32</sup> because iminopnictoranes are isoelectronic to ylides. However, there is an essential difference in the energy of reaction; the reactions of ylides are more exothermic than those of iminopnictoranes. This apparently originates from the difference in the stabilities that were evaluated by using hydrogen internal transfers. Ylides were estimated to be relatively less stable than iminopnictoranes.

Even the Corey–Chaykovsky reaction of P ylide is exothermic. The large exothermicity of the ylide Corey–Chaykovsky reaction directly results in the low activation energy. Consequently, the Corey–Chaykovsky reactions of ylides could take place easily and actually have been observed. The activation energies at the MP2 level were reported to be 15.6, 8.2, 5.2, and 7.4 kcal/mol for P, As, Sb, and Bi, respectively.<sup>32</sup>

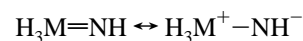
The Wittig reactions of ylides are more than 11 kcal/mol more exothermic than the aza-Wittig reaction. For  $M = P$ , it is 28 kcal/mol more exothermic. In this reaction, the rate-determining step starts from the intermediate I2. Therefore, the overall exothermicity is not directly related to the activation energy of the rate-determining step. The activation energies of normal Wittig reactions that have been reported (P (25.7 kcal/mol), As (30.9), Sb (34.0), Bi (34.9))<sup>32</sup> at the MP2 level) are close to those of the aza-Wittig reaction. Though the reactivity order is the same, the activation energies of the latter are smaller, compared with those of the former. The dipole–dipole interactions between polar  $H_2C=NH$  and  $H_3M=O$  presumably contributes to the lower barrier, whereas in the Wittig reaction, one of the interacting fragments is nonpolar  $H_2C=CH_2$ .

**Effect of the Electron Correlation.** The calculations with the MP perturbation theory up to MP4(SDTQ) and those by QCISD(T) with the DZ-d basis set at the MP2/DZ-d optimized geometries were performed to check the effect of electron correlation. The results are displayed in Figure 2 as potential energy surfaces. Comparison of the RHF results with those by the other methods shows that the influence of the electron correlations on the relative energies for each stationary point and for different M atoms are quite important. The difference is not so large between MP4(SDTQ) and QCISD(T). Indeed, the MP2 level, by which the relative energies are close to those by the more sophisticated method, is good enough to get the proper energies and geometries.

## Summary

This work investigates the geometries and bonding nature of iminopnictoranes and the mechanism of their reactions with formaldehyde as a model reaction system. Our findings are as follows.

There are two possible canonical structures for iminopnictoranes:



The population analysis has shown that between the two canonical forms, the ionic one is predominant, consistent with the electronegativity consideration and the barrier to internal rotation. However, the ratio of the M=N bond length to the M–N bond length in  $H_2M-NH_2$  shows that the M=N bond has a double bond character. The M–H bond lengths have shown that the  $n-\sigma^*$  negative hyperconjugation that was recently proposed makes a contribution to this double bond character. Because of their smaller electronegativity, the negative hyperconjugation in the iminopnictoranes with heavier M is harder to take place, resulting in the smaller double bond character. The bond length ratio as well as the barrier to the internal rotation demonstrated that the double bond character in the M=N bonds is smaller than that in the ylides, consistent with the larger electronegativity of the nitrogen atom, which results in the weak hyperconjugation.

The relative stability of iminopnictoranes, as well as ylides, that was calculated as the energy of internal hydrogen transfer shows that iminopnictoranes are thermodynamically more stable than ylides and that the stability decreases with going down the rows in the periodic table (P > As > Sb ~ Bi). This order of the stability for iminopnictoranes, as well as the same order for ylides, affects the features of the potential energy profiles of the reactions. Also, the order for the pnictogen oxides,  $H_3M=O$ , isoelectronic to  $H_3M=NH$  as well as  $H_3M=CH_2$ , was estimated to be the same.

The potential energy profiles were investigated for aza-Wittig and Corey–Chaykovsky-type reactions. The profiles are qualitatively similar to those for the reactions of the isoelectronic ylides. In the aza-Wittig reaction, there are four-membered cyclic intermediates with hypervalent pnictogens. The reaction from this intermediate, giving the pnictogen oxide and imine, has a high barrier and is rate-determining. The activation energies of this step is in the order P < As < Sb < Bi. Since the product of this step is pnictogen oxide  $H_3M=O$ , this is in the reverse order as the relative stabilities for  $H_3M=X$  (X = NH, O,  $CH_2$ ) according to the Hammond principle. In the Corey–Chaykovsky-type reaction leading to  $MH_3$  and azaoxaziridine, the order of the activation energies is P > As > Sb > Bi, the same as that of the stability order of the reactants



and opposite of that for the aza-Wittig reaction. Since this reaction transforms iminopnictoranes to normal valent compounds, according to the Hammond principle, the activation energy is in fact in the same order as the stability of iminopnictoranes. The Corey–Chaykovsky-type reaction of the most reactive iminopnictorane, with  $M = \text{Bi}$ , is thermodynamically and kinetically more favorable than the aza-Wittig reaction. Therefore, though the Corey–Chaykovsky-type reaction has not been reported for pnictogens, the calculations predict that for

iminobismorane, if prepared, the Corey–Chaykovsky-type  $S_N2$  reaction would take place.

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