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Gas-Phase Chemistry of Ethyl and Vinyl Amines, Phosphines, and Arsines: A DFT Study of the Structure and Stability of Their Cu$^+$ Complexes

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The B3LYP density functional approach has been used to calculate the Cu$^+$ binding energies of ethyl and vinyl amines, phosphines, and arsines. Geometries were fully optimized at the B3LYP/6-311G(d,p) level, and the final energies were obtained in B3LYP/6-311+G(2df,2p) single-point calculations. Significant differences between nitrogen-, phosphorus-, and arsenic-containing compounds have been found. For ethyl derivatives, the global minimum corresponds to the attachment of Cu$^+$ to the heteroatom. However, whereas for P and As derivatives of agostic complexes in which the metal cation interacts with the hydrogen atoms of the XH_2 or the CH_2 groups are found to be stable, they are not for ethylamine. For vinylamine, attachment to C_β is favored with respect to attachment to the heteroatom, whereas vinylphosphine and vinylarsine behave as P and As bases, respectively. The Cu$^+$ basicity trends also differ from those found for the corresponding proton affinities. Thus, although ethylamine is more basic than ethylphosphine and ethylarsine when the reference acid is H$^+$, ethylphosphine is the most basic compound when the reference acid is Cu$^+$. For the vinyl derivatives, the Cu$^+$ binding energies follow the trend P > As > N when only attachment to the heteroatom is considered, whereas the proton affinities follow the sequence N > P > As.

Introduction

The synthesis of ethyl arsines, vinylphosphine, and vinyl arsines[1,2] together with the recent experimental measurements of their gas-phase basicity and acidity[3,4] as well as spectroscopic properties[5,6] has given some new insights into the chemistry of the group VA elements and especially into the chemistry of As-containing compounds. These studies have shown that α,β unsaturated amines present a different reactivity than phosphines and arsines.[4] It is well established that enamines and ethynylamines are β-carbon bases.[7,8] Conversely, the corresponding phosphine analogues protonate preferentially at the heteroatom.[4] Arsines behave essentially as phosphines, except that protonation at the α-carbon competes with protonation at the heteroatom.[4]

Following these studies on the gas-phase reactivity of group VA derivatives, it is of interest to know the basicity trends when the reference acid is different from H$^+$. In this respect, Cu$^+$ represents a case in which the interaction still presents high covalent character.[9] However, there is great interest in the study of the interaction of neutral molecules with this metal monocation in areas such as biochemistry[10−18] or environmental chemistry, where knowledge of the nature of the interactions and the reactivity with metal cations is of relevance.[19−22] In our group, we have been interested recently in the study of Cu$^+$ binding energies[23,24] as well as in gas-phase reactions between Cu$^+$ and different organic bases that can be good models of more complicated biochemical systems.[9,25−27] In particular, the Cu$^+$ binding energies to sp, sp^2, and sp^3 nitrogen-, phosporous-, and arsenic-containing bases (XH_3, $H_2C{=}XH$, and $HC{\equiv}X$ (X = N, P, As)) show interesting trends[28] that clearly discriminate N- from P- and As-containing compounds. In the present study, we aim to extend this investigation to ethyl and vinyl amines, phosphines, and arsines, whose gas-phase proton affinities and acidities were also reported recently.[4] It is also interesting that similar investigations have been performed with group IVA analogues (ethyl and vinyl alkanes, silanes, and germanes),[29] and quite recently their reactivity toward Cu$^+$ has been also considered.[24] This latter study shows that in the case of Cu$^+$ complexes agostic interactions between the metal cation and the XH_3 group (X = C, Si, Ge) can play a crucial role. For this reason, one of the objectives of the present work will be to find out whether similar agostic interactions could lead to stable structures when the heteroatom belongs to the VA group and therefore has a greater electronegativity.

Computational Details

The structures of all the compounds under study have been obtained by using density functional theory (DFT). In particular, the B3LYP functional, which combines the Becke three-parameter nonlocal hybrid exchange potential[30] and the nonlocal correlation functional of Lee, Yang, and Parr,[31] was used in all calculations. The basis set used in the geometry optimizations was 6-311G(d,p) for all atoms except Cu$^+$, where the basis set of Watchers and Hay was employed.[32,33] The vibrational frequencies were calculated at the same level of theory in order to evaluate the zero-point energy (ZPE) correction and to determine whether the structures correspond to true minima of the potential energy surface (PES) or to transition states (TS).

Final energies have been evaluated by using the same functional combined with the 6-311+G(2df,2p) basis set for all atoms except Cu$^+$, where the (14s 9p 5d/9s 5p 3d) basis set of Watchers and Hay, supplemented with a set of (1s 2p 1d) diffuse functions, with two sets of f functions, and one set of g functions, was used.

Previous theoretical studies have established that the B3LYP functional, combined with similar basis sets, yields structures and energies comparable to those obtained at the G2 level of theory for a large variety of Cu$^+$ complexes.[9,23,25,26] Moreover, in some specific cases, B3LYP results are better than those

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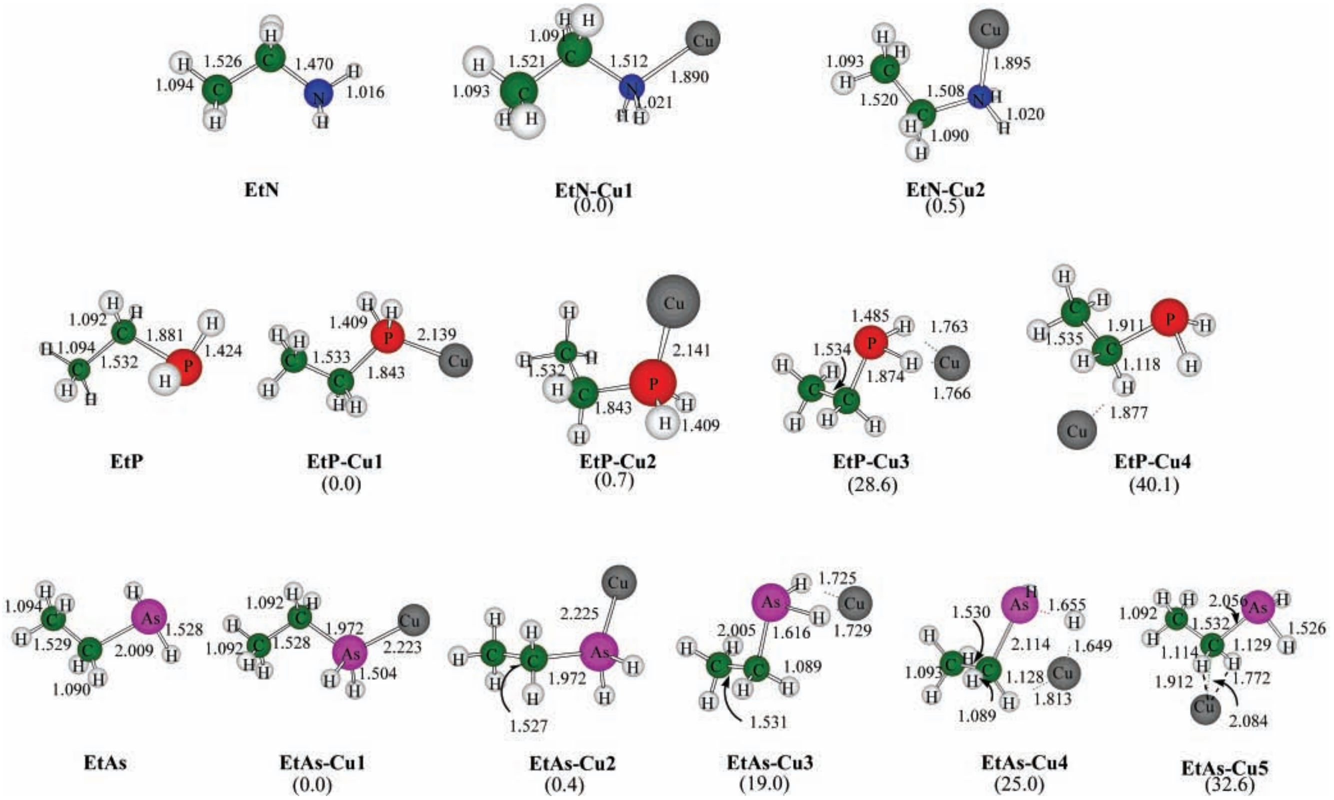


Figure 1. Structures of $H_3C-CH_2-XH_2$ (X = N, P, As) compounds and their Cu^+ complexes obtained at the B3LYP/6-311G(d,p) level of theory. Distances are given in Å, and angles are given in degrees. Numbers in parentheses corresponds to the relative stability in kcal/mol.

obtained at the MP2 level or by using composite theories such as G2 because of the existence of instabilities in the HF wave function or because of the poor convergence of the Moller−Plesset series.[23,34,35] It is important to note that these findings are based on previous studies that include systems containing N, P, or As as the basic center. For instance, the evaluated Cu^+ binding energy[24] for NH_3 at the B3LYP level differs by only 0.4 kcal/mol from the experimental value. Similar B3LYP calculations also reproduced the experimental proton affinities of ethyl, vinyl, and ethynyl phospines and arsines within less than 3 kcal/mol.[3−4]

The corresponding Cu^+ binding energies, D_0, were evaluated by subtracting from the energy of the complex the energy of the neutral and the energy of Cu^+ after including the corresponding ZPE corrections, which were scaled by the empirical factor 0.9806.[36]

To analyze the characteristics of the bonds in the different compounds and to know how they are modified upon complex formation, we have used the atoms in molecules (AIM) theory of Bader.[37] AIM theory permits us to define the bonds in the molecule by locating the critical points of the charge density. In particular, the bond critical points (bcp) and their associated bond paths permit us to define the network of bonds in the molecule and their characteristics. This feature is especially relevant when dealing with nonclassical structures, as is the case for the agostic bonds. However, the analysis of the Laplacian of the charge density ($\nabla^2\rho(\mathbf{r})$) permits us to classify the interaction as covalent (regions presenting negative values of $\nabla^2\rho(\mathbf{r})$ or electrostatic (regions presenting positive values of ($\nabla^2\rho(\mathbf{r})$). We have also made use of natural bond orbital (NBO) analysis[38] to get reliable charge distributions and to evaluate the intramolecular orbital interactions involved in agostic bonding. In particular, NBO analysis permits us to analyze quantitatively the donation of charge from occupied to vacant orbitals.

Calculations have been performed by using the Gaussian 98 suite of programs[39] and the AIMPAC package.[40]

Results and Discussion

Structures and Relative Stabilities of Ethyl Derivatives. The structures of ethylamine (**EtN**), ethylphosphine (**EtP**), and ethylarsine (**EtAs**) as well as those of their Cu^+ complexes and their relative stabilities are given in Figure 1. Their total energies and the Cu^+ binding energies are summarized in Table 1. The most stable forms correspond to "classical" structures in which Cu^+ is attached to the heteroatom trans with respect to the CH_3 group. The Cu^+-X (X = N, P, As) interaction produces a noticeable distortion of the bonds of the neutral compound, which depends on the electronegativity of the heteroatom. Thus, in agreement with the bond activation reinforcement (BAR) rule,[35] when X is more electronegative than C (as in **EtN**), the C−X bond becomes weaker, whereas when X is less electronegative than C (as in **EtP** or **EtAs**), a reinforcement of the X−C bond is observed. Consistently, a perusal of the vibrational frequencies shows that the X−C stretching frequency is red-shifted by 232 cm^{-1} in the case of **EtN** upon attachment of Cu^+ on the heteroatom, whereas it is blue-shifted by 25 and 15 cm^{-1} in the cases of **EtP** and **EtAs**, respectively.

The existence of a heteroatom bearing a lone pair makes this position the most suitable one for the attack of Cu^+, but, quite interestingly, in the case of **EtP** and **EtAs**, there exist other nonclassical local minima in which Cu^+ interacts with two hydrogens of the molecule. In the case of **EtP**, two different complexes are obtained, namely, **EtP−Cu3** and **EtP−Cu4**. In the former, Cu^+ interacts with the two hydrogens of the PH_2 group, whereas in the latter, it does so with the two hydrogens of the CH_2 group, the former being more stable. In the case of **EtAs**, in addition to these two nonclassical structures, namely, **EtAs−Cu3** and **EtAs−Cu5**, there also exists a third minimum

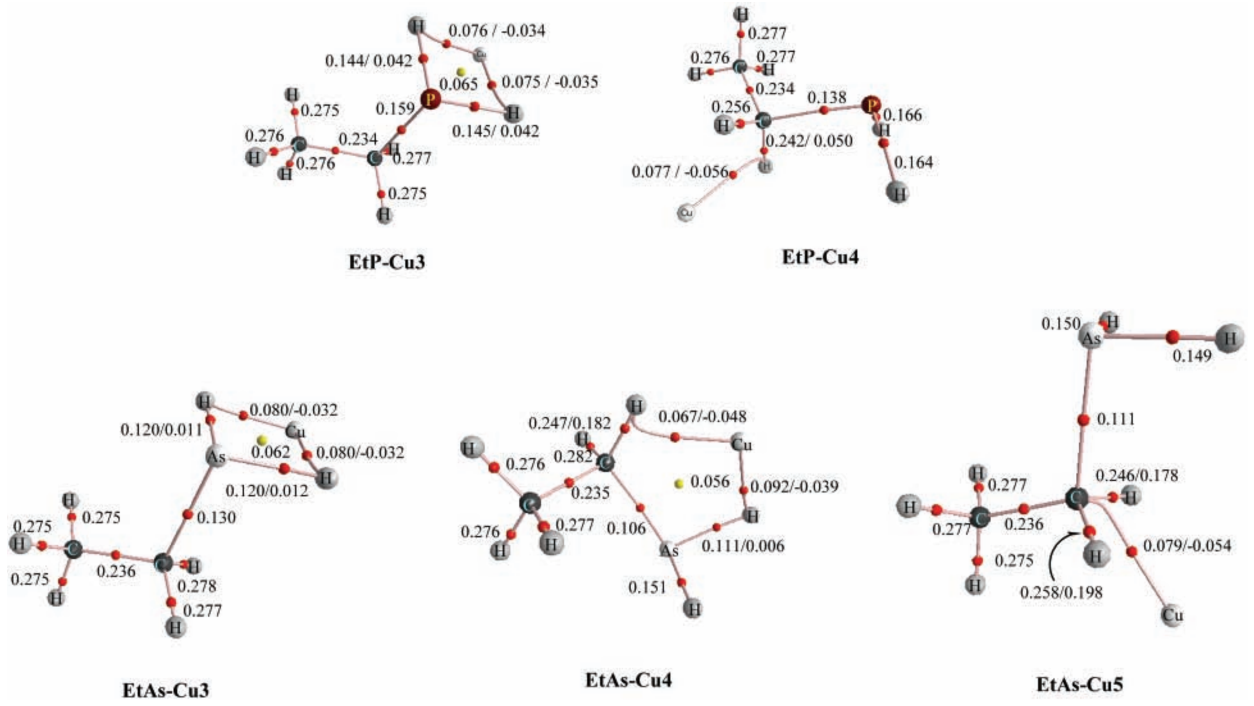
TABLE 1: Total Energies (*E*), Zero-Point Energies (ZPE), and Cu^+ Binding Energies (D_0) for All Compounds under Study

compound	*E* (au) 6-311+G(2df,2p)	ZPE (au) 6-311G(d,p)	D_0 (kcal/mol)
EtN	−135.22942	0.09239	
EtN−Cu1	−1775.50907	0.09612	62.3
EtN−Cu2	−1775.50834	0.09613	61.8
EtP	−421.83409	0.08300	
EtP−Cu1	−2062.11819	0.08563	65.7
EtP−Cu2	−2062.11716	0.08565	65.1
EtP−Cu3	−2062.07033	0.08323	37.2
EtP−Cu4	−2062.05133	0.08260	25.6
EtAs	−2316.32998	0.08081	
EtAs−Cu1	−3956.60612	0.08292	61.0
EtAs−Cu2	−3956.60568	0.08310	60.7
EtAs−Cu3	−3956.57375	0.08076	42.1
EtAs−Cu4	−3956.56370	0.08085	35.7
EtAs−Cu5	−3956.55140	0.08018	28.4
ViN	−134.00377	0.06868	
ViN−Cu1	−1774.28393	0.07199	62.8
ViN−Cu2	−1774.26786	0.07220	52.6
ViN−Cu3	−1774.26526	0.07150	51.4
ViN−Cu4 (TS1)	−1774.26063	0.07154	48.9
ViP	−420.59783	0.05952	
ViP−Cu1	−2060.87648	0.06224	62.2
ViP−Cu2	−2060.87603	0.06225	62.0
ViP−Cu3	−2060.85162	0.06198	46.8
ViP−Cu4	−2060.84977	0.06153	45.9
ViP−Cu5 (TS1)	−2060.85395	0.06073	49.0
ViAs	−2315.09195	0.05750	
ViAs−Cu1	−3955.36303	0.05964	57.9
ViAs−Cu2	−3955.36270	0.05955	57.7
ViAs−Cu3	−3955.34781	0.05976	48.2
ViAs−Cu4	−3955.34472	0.05959	46.4
ViAs−Cu5 (TS1)	−3955.34282	0.05848	45.9

of the PES (**EtAs−Cu4**) in which Cu^+ bridges between one of the hydrogens of the CH_2 group and another hydrogen of the AsH_2 group.

These $Cu^+−H−X$ (X = P, As) interactions are similar to what Brookhart and Green called agostic interactions in transition-metal complexes. Indeed, the name agostic was introduced by Brookhart and Green[41] to describe the interaction of the C−H bond with transition metals. This interaction is responsible for significant ^1H NMR chemical shifts to high field,[42] reduced NMR coupling constants,[42] low vibrational stretching frequencies,[43] short metal−hydrogen distances,[44] and significant lengthening of the C−H bonds interacting directly with the metal. Also, similar interactions have recently been found to be important for Si−H bonds in complexes involving neutral transition metals[45,46] and in complexes involving Co^+ and hydrocarbons.[47] Popelier and Logothetis[48] have recently proposed a characterization of these agostic bonds on the basis of a topological analysis of the charge density of the complex.

In our study, we have generalized the name agostic to describe not only the interactions between C−H and the metal but also the interactions between P−H or As−H bonds with the metal because, as we will see in the present study, the characteristics of both interactions are quite similar. It is worth noting that some of these complexes are quite stable. For instance, **EtAs−Cu3** is only 19.0 kcal/mol less stable than the global minimum, and it may play a significant role as far as the unimolecular loss of H_2, as often observed in the interaction of organic bases with metal monocations. In fact, as can been seen in Figure 1, the interaction with Cu^+ in the aforementioned agostic complexes leads to a significant lengthening of the CH, PH, or AsH bonds (by 0.02, 0.06, and 0.09 Å, respectively). However, in all cases, there is an accumulation of charge in the $Cu^+−H$ region that is mirrored in the existence of one or two bcps in that region, as illustrated in Figure 2. This Figure shows the molecular graphs obtained by locating the different bcps of the charge density and by generating the corresponding bond paths. Quite interestingly, the values of ρ (0.07−0.09 e/au^3) are almost double those reported by Popelier and Logothetis,[48] as typical of agostic linkages, but similar to those estimated for



EtP-Cu3 EtP-Cu4

EtAs-Cu3 EtAs-Cu4 EtAs-Cu5

Figure 2. Position of the bond critical points and bond paths for $H_3C−CH_2−XH_2$ (X = P, As)$−Cu^+$ complexes showing an agostic interaction between Cu^+ and the XH_2 or CH_2 group. For each critical point, the first number corresponds to the electron density (e/au^3); in the case of the bonds involved in the agostic interaction, the second number corresponds to the value of $\nabla^2\rho(r)$ (e/au^5).

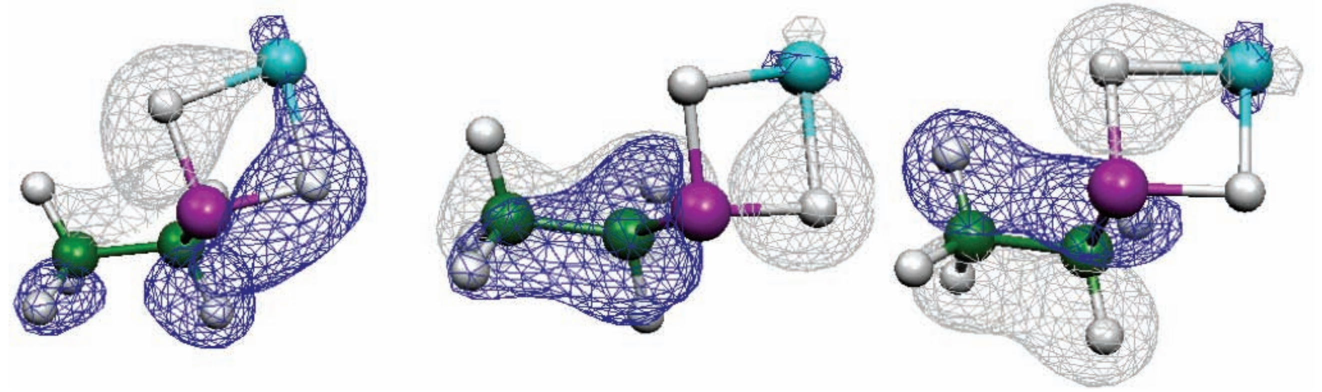


Figure 3. Molecular orbitals for complex **EtP−Cu3**. Only the occupied orbitals with bonding between the Cu^+ and the PH_2 group are shown.

TABLE 2: Second-Order Perturbation Theory Analysis of the Fock Matrix in the NBO Basis

	CH_3CH_2XH to Cu donation		Cu to CH_3CH_2XH donation	
compound	orbitals involved	orbital interaction energy (kcal/mol)	orbitals involved	orbital interaction energy (kcal/mol)
EtP−Cu3	σ (P−H_1) → 4s (Cu)	20.13	3d (Cu) → σ* (P−H_1)	8.90
	σ (P−H_2) → 4s (Cu)	20.08	3d (Cu) → $^{\sigma}$* (P−H_2)	8.82
EtP−Cu4	σ (C−H_1) → 4s (Cu)	10.91	3d (Cu) → σ* (C−H_1)	4.82
	σ (C−H_2) → 4s (Cu)	7.22	3d (Cu) → σ* (C−H_2)	3.17
			3s (Cu) → σ* (C−P)	2.72
EtAs−Cu3	σ (As−H_1) → 4s (Cu)	25.87	3d (Cu) → σ* (As−H_1)	5.63
	σ (As−H_2) → 4s (Cu)	26.06	3d (Cu) → σ* (As−H_2)	5.84
EtAs−Cu4	σ (As−H) → 4s (Cu)	33.33	3d (Cu) → σ* (As−H)	13.15
	σ (C−As) → 4s (Cu)	13.74	3d (Cu) → σ* (C−As)	4.48
	σ (C−H) → 4s (Cu)	12.85	3d (Cu) → σ* (C−H)	4.50
EtAs−Cu5	σ (C−H_1) → 4s (Cu)	10.63	3d (Cu) → σ* (C−H_1)	4.16
	σ (C−H_2) → 4s (Cu)	7.08	3d (Cu) → σ* (C−H_2)	1.61
			3s (Cu) → σ* (C−As)	3.33

Si- and Ge-containing compounds. Also, in our case, $\nabla^2\rho$ is negative rather than positive, indicating that these interactions are particularly strong when dealing with metal cations rather than with neutrals.

These agostic interactions are reflected in the existence of different occupied orbitals, in which a d orbital of the metal interacts with the σ (X−H) orbitals (see Figure 3). They are also reflected, in a consistent manner, in the second-order NBO analysis, which shows for all these complexes the existence of donation from a σ (X−H) (X = C, P, As) bonding orbital to a vacant 4s orbital of the metal and back-donation from a filled 3d orbital of Cu^+ to a σ* (X−H) antibonding orbital of the base (see Table 2). It is this back-donation that is responsible for the significant lengthening of the X−H bond. From a more quantitative point of view, it can be observed that these dative bonds are stronger for P and As than for C, in agreement with the differences between the Cu···HC and Cu···HP or Cu···HAs bond densities (See Figure 2) and with the relative stability of the different agostic complexes (see Table 1). Consistently, as illustrated in Table 3, the stretching frequencies of the X−H linkages involved in the agostic interaction are strongly shifted to the red (from 390 to 650 cm^{-1}).

The fact that the agostic interaction must involve an electron-rich X−H group, which is able to donate charge easily to the metal, explains why this interaction is favored in **EtAs** with respect to **EtP** (the corresponding Cu^+ binding energies are 42.1 and 37.2 kcal/mol) and why these complexes do not exist for **EtN**. By comparing the calculated binding energies of P- and As-containing complexes with the C-, Si- and Ge-containing analogues (propane (27.0 kcal/mol), ethylsilane (40.8 kcal/mol), and ethylgermane (42.9 kcal/mol)), one may conclude that the agostic interaction energies roughly follow the reverse order of the heteroatom electronegativity (C > P > As > Si ≈ Ge).

TABLE 3: Stretching Vibrational Frequencies (cm^{-1}) for the Bonds Involved in Agostic Interactions

	EtP	**EtP−Cu3**	**EtP−Cu4**
P−H stretching	2362	1971	2390
	2369	1987	2405
C−H stretching	3038	3053	2597
	3073	3117	2785
C−P stretching	630	621	634

	EtAs	**EtAs−Cu3**	**EtAs−Cu4**	**EtAs−Cu5**
As−H stretching	2172	1689	1515	2170
	2183	1700	2182	2193
C−H stretching	3048	3063	2646	2673
	3109	3127	3112	2844
C−As stretching	532	510	442	558

Structures and Relative Stabilities of Vinyl Derivatives. The structures of vinylamine (**ViN**), vinylphosphine (**ViP**), vinylarsine (**ViAs**), and their Cu^+ complexes are given in Figure 4. In these cases, Cu^+ attachment to the C═C double bond may compete with attachment to the heteroatom lone pair. In this respect, once more the nitrogen derivative, **ViN**, behaves differently with respect to the P- and As-containing systems, **ViP** and **ViAs**. The first conspicuous fact is that **ViN** is planar, whereas in **ViP** and **ViAs**, the PH_2 and AsH_2 groups are found to be highly pyramidal. The estimated energy barriers to go from the equilibrium conformation of **ViP** and **ViAs** to the planar structure are predicted to be sizeably high (28.0 and 31.9 kcal/mol respectively). The second important difference is that

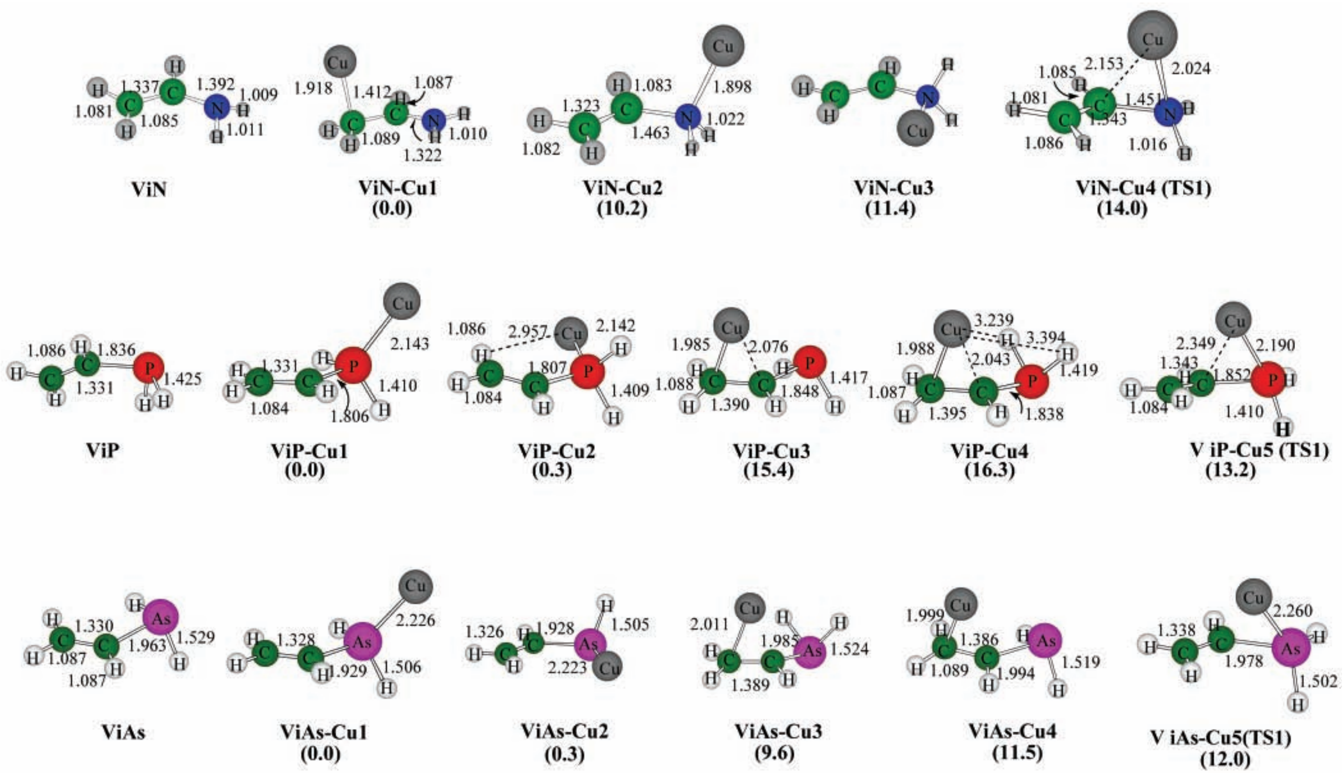


Figure 4. Structures of $H_2C{=}CH{-}XH_2$ (X = N, P, As) compounds and their Cu^+ complexes obtained at the B3LYP/6-311G(d,p) level of theory. Distances are given in Å, and angles are given in degrees. Numbers in parentheses corresponds to the relative stability in kcal/mol.

for **ViN** C_β is the most basic site for Cu^+ attachment whereas **ViP** and **ViAs** behave as P and As bases, respectively. Indeed, our results show that attachment of Cu^+ to the N atom of **ViN** is 10.2 kcal/mol less exothermic than attachment to C_β. It is also worth noting that in **ViN−Cu1** the NH_2 group remains planar, favoring the conjugation between the N lone pair and the π cloud, whereas N attachment leads to a significant pyrimidalization of the NH_2 group. The energy barrier connecting both local minima,**ViN−Cu1** and **ViN−Cu2**, is much lower (14.0 kcal/mol) than the Cu^+ binding energy (62.8 kcal/mol); therefore, both minima should be energetically accessible.

As mentioned above, in the case of **ViP** and **ViAs**, Cu^+ preferentially binds to the heteroatom. The interaction energy with the C═C π bond is about 10 kcal/mol lower. However, the energy barriers from these complexes (**ViP−Cu3** or **ViAs−Cu4**) to the global minima (**ViP−Cu1** or **ViAs−Cu1**) are extremely low (0.5 kcal/mol for **ViAs** and barrierless for **ViP** when ZPE is taken into account). As a consequence, at room temperature, only **ViP−Cu1** and likely **ViAs−Cu1** should be observed in the gas phase.

It is also worth noting that, in contrast with what has been found for the corresponding saturated analogues, no agostic complexes are found to be stable for the unsaturated systems because they collapse to the heteroatom-attached complexes. This can be understood if one takes into account that the $H_2C{=}CH{-}$ group is more electronegative than the $H_3C{-}CH_2{-}$ group. Accordingly, the XH_2 substituent, when bound to an unsaturated moiety, becomes a poorer electron donor, and their hydrogen atoms have also a lower charge density.

All complexes in which Cu^+ is attached to the heteroatom present two different conformers that are very close in energy but differ in the relative position of the metal cation with respect to the plane that contains the $H_2C{=}CH$ moiety. For P and As derivatives, the π complexes also exhibit two different conformations. Although they are also very close in energy, for P derivatives, the conformer in which the XH_2 group is anti with respect to the metal cation is more stable than the syn conformer. For As-containing complexes, the reverse stability order is predicted, reflecting a more stabilizing interaction between Cu and the hydrogen atoms of the AsH_2 group.

Cu^+ Versus H^+ Basicities. One of the aims of the present study is to compare Cu^+ versus H^+ gas-phase basicities of the ethyl and vinyl derivatives. Let us consider first the case in which the basic center is the heteroatom. The gas-phase proton affinity decreases as **EtN** > **EtP** > **EtAs** (the proton affinities are 218.5, 207.0, and 199.2 kcal/mol, respectively).[4] For Cu^+, the estimated binding energies, D_0, follow the trend **EtP** > **EtN** > **EtAs** (65.0, 61.8, and 60.7 kcal/mol, respectively). Therefore, **EtN** is the most basic compound with respect to H^+, but it is not when the reference acid is Cu^+.

Similar differences are found for the vinyl derivatives. If only attachment at the heteroatom is considered, the proton affinities decrease as **ViN** > **ViP** > **ViAs** (220.9, 202.9, and 199.2 kcal/mol, respectively),[4] whereas the corresponding Cu^+ biding energies follow a different trend: **ViP** > **ViAs** > **ViN** (62.2, 57.9, and 52.6 kcal/mol, respectively), the amine derivative being the least basic compound. The fact that in the case of **ViN** the most basic position is not N but C_β makes **ViN** slightly more basic with regard to Cu^+ (62.8 kcal/mol) than **ViP**.

At this point, it is also important to note that whereas vinylamine presents enhanced proton and Cu^+ affinities with respect to ethylamine, for phosphines and arsines, both proton and Cu^+ affinities are predicted to be higher for the saturated compounds.

Analogous dissimilarities are also observed as far as the nature of the most basic site is concerned. Depending on the basic site (X, C_α, or C_β), three structures are possible upon protonation. For **ViN**, N protonation is favored over C_β protonation by 14.7 kcal/mol, whereas, as we have seen above for Cu^+ attachment, the most basic center is C_β. For **ViP**, both Cu^+ and

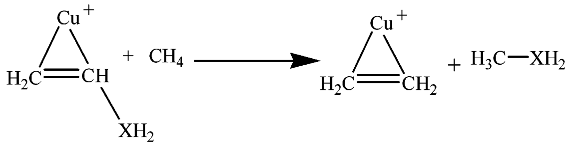
TABLE 4: Calculated Enthalpies for Isodesmic Reactions 1 and 2

X	Δ*H* (kcal/mol)
reaction 1	
N	+32.2
P	+8.8
As	+6.4
reaction 2	
N	−3.4
P	+10.1
As	+8.1

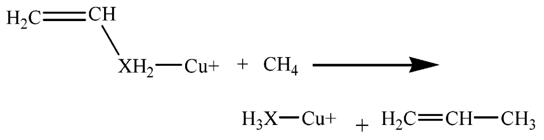
H^+ attach preferentially to P. Finally, for **ViAs**, Cu^+ attaches preferentially to As, whereas the C_α-protonated species is estimated to be only 0.1 kcal/mol more stable than the As-protonated species. Why does vinylamine behaves as a carbon base in the presence of reference acid is Cu^+ when vinylphosphine and vinylarsine behave as P and As bases, respectively? The geometrical changes observed upon Cu^+ association offer some clues to answer this question. As shown in Figure 4, Cu^+ attachment on C_β of vinylamine leads to a weakening of the C═C bond and to a concomitant reinforcement of the C−N linkage. Conversely, attachment to the nitrogen atom weakens the C−N bond but reinforces the C═C bond. So in both cases there are two opposite effects that, nevertheless, cannot be quantitatively equal. In fact, looking at the bond lengths, it seems apparent that the reinforcement of the C−N linkage in the first case is greater than the reinforcement of the C═C linkage in the second case, whereas the C−C weakening is smaller than the C−N weakening. This will be consistent with the enhanced stability of the C_β-attached complex.

For P and As derivatives, the situation is completely different. Whereas Cu^+ attachment to the heteroatom reinforces the C−X bond and does not perturb the C═C linkage significantly, attachment to the π system weakens both the C═C and the C−X bonds. Hence, in this case, one should expect the first complexes to be more stable.

These differences can be analyzed in a more quantitative way by using the following isodesmic reactions:



(1)



(2)

The first one measures the influence of the XH_2 substituent on the stabilization of Cu^+ complexes in which the metal cation interacts with the C═C double bond. The second measures the effect of the $H_2C{=}CH-$ group on the stability of complexes in which Cu^+ is attached to the XH_2 group. The enthalpies of these reactions, evaluated at the B3LYP/6-311+G(2df,2p) level of theory, have been summarized in Table 4.

The first conspicuous fact is that reaction 1 is found to be systematically endothermic, indicating that XH_2 (X = N, P, As) groups stabilize π complexes. Although this effect is four times larger for N than for P or As, this is not enough to explain the preference of amines to yield this kind of complex. Concomitantly, however, reaction 2 is found to be only endothermic for P- and A-containing compounds and exothermic for vinylamine. This implies that the unsaturated $H_2C{=}CH-$ moiety stabilizes X-attached Cu^+ complexes when X = P or As but destabilizes them when X = N. This is consistent with the fact that vinylamine has a N−Cu^+ binding energy (52.6 kcal/mol) that is smaller than that of ammonia (56.2 kcal/mol), whereas vinylphosphine and vinylarsine have Cu^+ binding energies (62.2 and 57.9 kcal/mol, respectively) that are higher than those of PH_3 (53.4 kcal/mol) and AsH_3 (49.3 kcal/mol).

In summary, the enhanced stability of the **ViN−Cu1** complex reflects the ability of the N lone pair to conjugate with the C═C π system, alleviating its electronic depletion upon Cu^+ association, whereas this conjugation is much less effective when P or As lone pairs are involved. Of course this conjugation disappears upon association at the heteroatom, but whereas this effect is very important in the case of the nitrogen derivative, whose NH_2 group strongly pyrimidalizes, it is much smaller for P and As derivatives where the pyrimidalization of XH_2 is already very large in the neutral system.

Conclusions

Our results show significant differences in the behavior of nitrogen bases with respect to their phosphorus- and arsenic-containing analogues. Although for $H_3C-CH_2-XH_2$ (X = N, P, As) compounds the global minimum corresponds, systematically, to the attachment of Cu^+ to the heteroatom, only for P- and As-derivative agostic complexes, in which the metal cation interacts with the hydrogen atoms of the XH_2 or the CH_2 groups, were there found to be local minima of the potential energy surface. These nonclassical linkages are characterized by charge densities at the bond critical points that are larger than those typically associated with closed-shell interactions and lead to a significant weakening of the X−H bonds involved.

Dissimilarities between N and P or As are also significant as far as the unsaturated compounds are concerned. For vinylamine, attachment to C_β is favored with respect to attachment to the heteroatom, whereas vinylphosphine and vinylarsine behave as P and As bases, respectively. This is a consequence of the fact that whereas the amino group strongly stabilizes the complexes in which Cu^+ interacts with the C═C π system this effect is much smaller when the substituent is a PH_2 or an AsH_2 group. Concomitantly, attachment to the heteroatom is favored by the $H_2C{=}CH-$ unsaturated group only when the heteroatom is P or As.

The Cu^+ basicity trends also differ from the corresponding proton affinity trends. Thus, although ethylamine is more basic than ethylphosphine and ethylarsine when the reference acid is H^+, ethylphosphine is the most basic compound when the reference acid is Cu^+. For the vinyl derivatives, the Cu^+ binding energies follow the trend P > As > N when only attachment to the heteroatom is considered, in contrast with the proton affinities that follow the sequence N > P > As.

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