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Agostic vs *π*-Interactions in Complexes of Ethynylsilanes and Ethynylgermanes with Cu^+ in the Gas Phase

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The gas-phase interaction of $HC{\equiv}C-XH_3$ (X = C, Si, and Ge) with Cu^+ has been investigated through the use of high-level density functional theory methods. The structures of the corresponding Cu^+ complexes were optimized at the B3LYP/6-311G(d,p) level of theory, while the final energies were obtained in single-point B3LYP/6-311+G(2df,2p) calculations. In all cases, it is found that complexes presenting nonconventional (agostic) interactions with the XH_3 terminal group lie slightly higher in energy than conventional π-complexes. An analysis of their charge density clearly indicates that these interactions have a nonnegligible covalent character and that they are favored by the hydride character of the hydrogen atoms of the XH_3 substituent. Accordingly, substitution of some of these hydrogens by electron releasing groups enhances the stability of the corresponding agostic complex which becomes very close in stability to π complexes. These agostic interactions lead to a significant weakening of the X−H linkage involved, reflected in a very large red shifting of the X−H stretching frequency.

Introduction

The interaction of metal monocations with neutral molecules in the gas phase has been the subject of many experimental and theoretical studies in the past decades of the last century.[1−6] This interest has been motivated by the large number of processes in chemistry, biochemistry, or environmental chemistry, in which these interactions are crucial. As a consequence of these efforts, it seems well-established that these interactions are essentially electrostatic for complexes involving alkali metal monocations,[7−10] although polarization effects are crucial to explain the formation of nonclassic structures in which the metal interacts simultaneously with two or more basic sites of the neutral molecule.[11] The situation is somewhat slightly different when dealing with transition metal monocations. Although it has been generally assume that these interactions are also mostly electrostatic,[12] there are several evidences that indicate that they have a nonnegligible covalent nature.[13,14] For example, most of the complexes involving Cu^+ or Ni^+ exhibit structures which resemble closely those of the corresponding protonated species, where a true covalent bond is formed between the basic center and the proton, which is not the case for analogous complexes with alkali metal monocations. On the other hand, the Cu^+ or Ni^+ binding energies are higher than those of alkali metal monocations.[3,15−17] Consistently, the charge densities at the bond critical point between the basic site and the metal are also higher, reflecting a propensity to accumulate electronic charge in the bonding region, which should not occur in typical ionic bonds. But perhaps the most interesting peculiarity of transition metal monocations is their ability to form agostic bonds. This name was used for the first time by Brookart and Green,[18] to designate interactions between transition metal cations and C−H bonds which lead to unusual low field shifts in the ^{1}H NMR spectrum,[19] C−H bond lengthening,[20] reduced C−H stretching frequencies,[20] and remarkably short metal−hydrogen distances.[21] These nonconventional linkages were described by Cotton et al.[21] as three-center-two electron bonds, similar to the ones responsible for the bonding in diborane or for the bonding in many protonated alkanes[22−25] or in the protonated form of P_4,[26] where the proton bridges between two neighbor basic centers. More recently, an alternative picture in terms of a donation from a X−Y σ bonding orbital to a vacant metal orbital, followed by a back-donation from a filled metal d orbital to the X−Y σ* antibonding orbital was proposed.[27] As a consequence, Nikonov et al.[28] considered more appropriate the term three-center-*n*-electrons ($2 \leq n < 4$) to describe these bonds. An interesting analysis of these nonclassical bonds in terms of the atoms in molecules (AIM) theory has been reported recently by Popelier.[29]

In a recent paper[30] we have shown that these interactions are not exclusive of neutral transition metals and C−H bonds. Actually, they are particularly strong when dealing with transition metal cations and X−H bonds, in which X is an atom less electronegative than carbon, such as Si and Ge. Indeed, the large strength of these agostic interactions explains why the Cu^+ BEs of ethylsilane and ethylgermane are much larger than that of propane. Also, the most stable Cu^+ complex of vinylsilane and vinylgermane ($H_2C{=}CH-XH_3$; X = Si and Ge) exhibits a nonconventional structure in which Cu^+ interacts simultaneously with one of the carbon atoms of the unsaturated moiety and one of the X−H bonds of the XH_3 substituent, whereas the conventional π complex, which is the global minimum of the PES in the case of propene, lies higher in energy.

The aim of this paper is to analyze the strength of these interactions when the unsaturated base contains a C≡C triple bond, which implies an increase of the electronegativity of the group, which should affect the strength of the Cu^+-XH agostic interaction. For this purpose we have investigated the structure and relative stability of the complexes between $HC{\equiv}C-XH_3$ (X = C, Si, Ge) and Cu^+. To this initial set, and in order to gain further insight into the nature of the agostic interaction we have added the $CH_3-C{\equiv}C-XH_3$ and the $H-C{\equiv}C-XH_2$-CH_3 (X = Si and Ge) derivatives.

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This study has another added interest, since very little is known about the properties and reactivity of these α,β-unsaturated silanes and germanes in the gas phase, because some of them are of low stability and their synthesis was described only very recently.[31,32] As a consequence, their gas-phase acidities[33] and basicities[34] were obtained for the first time only one year ago. Clear differences, as far as these intrinsic properties are concerned, were found between Si and Ge-containing systems and their C-containing analogues. In this respect it would be useful to compare their behavior with respect to Cu^+ with that exhibit when the reference acid is H^+. Finally, the results presented along this paper may guide future experimental studies and will provide reliable estimates of the Cu^+ binding energies of these compounds.

Computational Details

The geometries and the harmonic vibrational frequencies of the different species under consideration have been optimized by using the hybrid density functional B3LYP method, which includes the Becke's three-parameter nonlocal hybrid exchange potential[35] and the nonlocal correlation functional of Lee, Yang, and Parr.[36] All these calculations were performed using the all electron basis of Wachters−Hay[37,38] (6-311G*) for Cu and the 6-31G* basis set for the remaining atoms of the system. The corresponding zero-point energies (ZPE) were scaled by the empirical factor 0.9806.[39] The final energies of the different species under study were obtained in DFT/6-311+G(2df,2p) single-point calculations using the aforementioned DFT optimized geometries. For Cu the basis set 6-311+G(2df,2p) corresponds actually to the (14s9p5d/9s5p3d) Wachters−Hay[37,38] basis supplemented with a set of (1s2p1d) diffuse functions and with two sets of f functions (rather than d) and one set of g functions (rather than f).

In contrast with the most commonly used ab initio approaches, which exhibit very often instabilities of the HF wave function and poor convergency of the MPn series,[40−42] the B3LYP density functional theory approach has been proved to be very well-suited for the description of Cu^+ complexes, and in general, the calculated Cu^+ binding energies are in fairly good agreement with the experimental values.[40,43] On the other hand, in general, geometries obtained using the aforementioned DFT method are in fairly good agreement with experimental values,[4,5,44−52] and the harmonic vibrational frequencies are closer to experiment than those obtained by using other correlated methods such as MP2.[53,54]

The corresponding Cu^+ binding energies D_0 were evaluated by subtracting from the energy of the complex the energy of the neutral and that of Cu^+, after including the corresponding ZPE corrections.

The Cu^+-XH agostic interactions will be characterized by means of two different theoretical techniques, the AIM theory of Bader[55] and the natural bond orbital (NBO) analysis of Reinhold et al.[56] The first of these approaches will allow us to locate the corresponding bond critical points (bcps), whose electron density is a good measure of the strength of the linkage. The covalent nature of the interaction will be assessed by means of the contour maps of the energy density. We have shown that covalent bonding regions coincide systematically with areas of the energy density contour map where this magnitude is negative. Conversely, typical ionic linkages are associated with regions where the energy density is clearly positive. The NBO approach will allow us to obtain reliable charge distributions, and quantitatively evaluate the intramolecular attractive orbital interactions involved in the agostic interactions. For this purpose the donation from occupied orbitals of the neutral toward vacant orbitals of Cu^+, and/or from occupied orbitals of Cu^+, toward antibonding orbitals of the neutral will be estimated. This analysis will be complemented with that carried out in terms of the lengthening or shortening of the bond lengths and in terms of the shifting of the corresponding stretching frequencies.

TABLE 1: Total Energies (*E*, hartrees), Zero-Point Energies (ZPE, hartrees) and Cu^+ Binding Energies (D_0, kcal mol^{-1}) of $HC{\equiv}CXH_3$, $CH_3C{\equiv}CXH_3$, and $HC{\equiv}CXH_2(CH_3)$ (X = C, Si, and Ge) Compounds and Their Cu^+ Complexes

	E[a]	ZPE[b]	D_0 (kcal/mol)[c]
propyne	−116.7007594	0.055478	
C1	−1756.9564527	0.056419	**48.9**
C2	−1756.9193586	0.056070	25.8
C3	−1756.9056844	0.055486	17.6
ethynylsilane	−368.1025600	0.043455	
Si1	−2008.3554730	0.044264	**47.2**
Si2	−2008.3327418	0.043975	33.1
Si3	−2008.3341415	0.044444	33.7
Si4	−2008.3525883	0.044925	45.0
ethynylgermane	−2155.5814300	0.041849	
Ge1	−3795.8390242	0.042467	**50.3**
Ge2	−3795.8210642	0.042069	39.2
Ge3	−3795.8115310	0.042068	33.2
Ge4	−3795.8340446	0.042806	46.9
methyl derivatives			
Me−Si	−407.4426692	0.0717334	
Me−Si1	−2047.7037318	0.0726505	**52.2**
Me−Si2	−2047.7008080	0.0731002	50.1
Si−Me	−407.4468623	0.0726512	
Si−Me1	−2047.7059912	0.0733873	**51.1**
Si−Me2	−2047.7057724	0.0738269	50.7
Me−Ge	−2194.9208561	0.0700662	
Me−Ge1	−3835.1866159	0.0708621	**55.3**
Me−Ge2	−3835.1809924	0.0709033	51.7
Ge−Me	−2194.9212628	0.0710601	
Ge−Me1	−3835.1848244	0.0717398	**54.0**
Ge−Me2	−3835.1824808	0.0718542	52.4

[a] Calculated at the B3LYP/6-311+G(2df,2p) level. [b] Calculated at the B3LYP/6-311G(d,p) level. [c] Calculated at the B3LYP/6-311+G(2df,2p) level including ZPE corrections (see text).

All calculations have been carried out using the Gaussian-98 suite of programs.[57]

Results and Discussion

Although it seems well-established that the interaction of unsaturated hydrocarbons, such as ethylene or acetylene, with transition metal monocations from V^+ through Cu^+ leads to complexes where the metal cation sits at the bond midpoint, yielding typical C_{2v} π complexes,[12] we have recently shown that this is not necessary the case when the unsaturated compound presents XH_3 (X = Si and Ge) susbtituents. In these cases, the simultaneous interaction of the metal cation with the π system and the substituent yields the global minimum of the potential energy surface. Hence, in the present study we have considered not only the attachment to the C≡C bond but to all possible active sites of the neutral.

Structures, Relative Stabilities, and Bonding. The structures of the different $HC{\equiv}CXH_3$ (X = C, Si, and Ge) unsaturated species as well as those of their Cu^+ complexes are given in Figure 1. Their total energies are summarized in Table 1. Table 1 contains also the calculated binding energies D_0.

The attachment of Cu^+ to propyne leads to three different cations, the π complex **C1** being the global minimum of the PES. Attachment of Cu^+ to the β-carbon of the triple bond collapses to the global minimum, while attachment to the

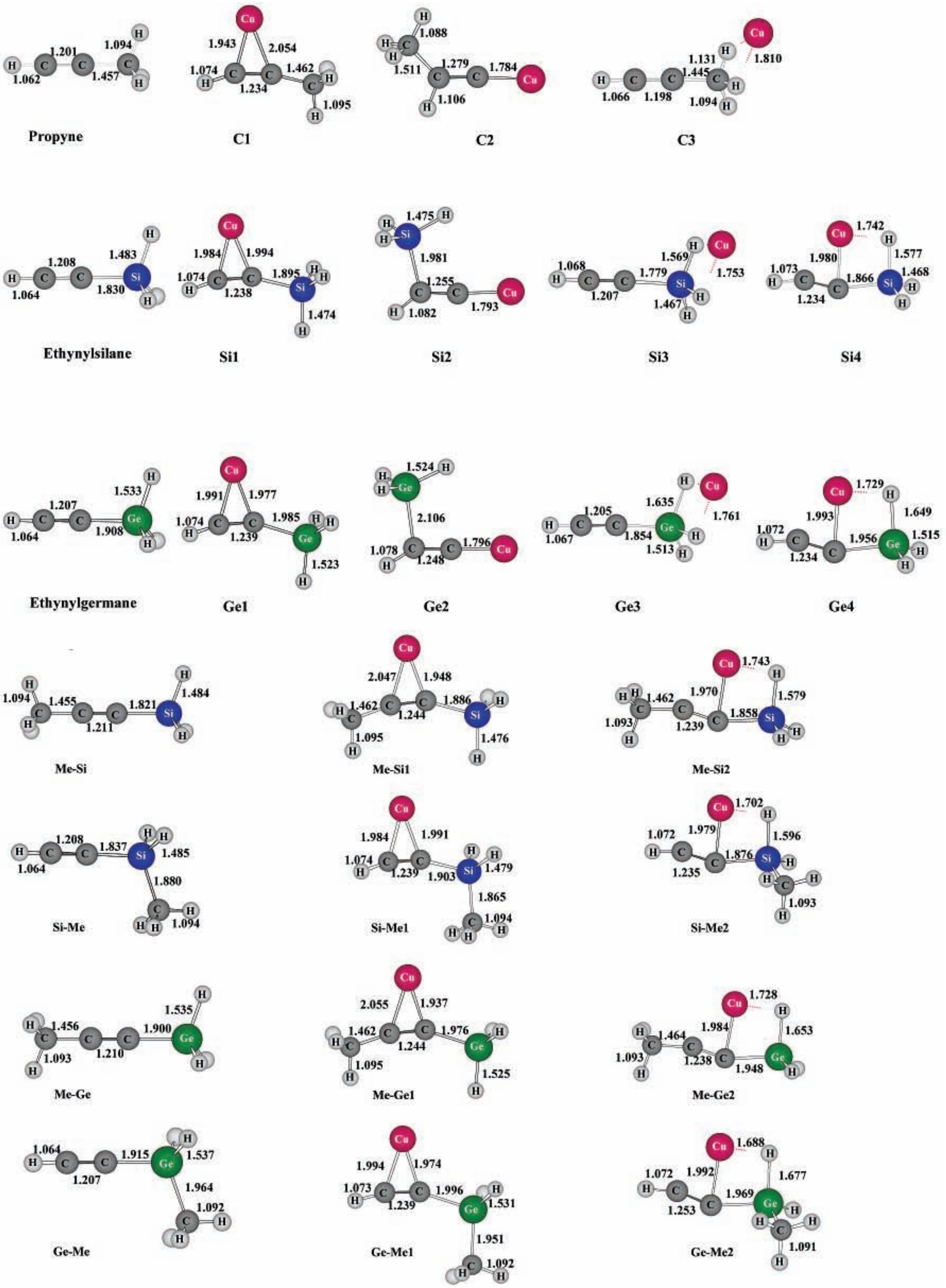


Figure 1. B3LYP/6-311G(d,p) optimized geometries of $HC{\equiv}C{-}XH_3$, $CH_3{-}C{\equiv}C{-}XH_3$ and the $H{-}C{\equiv}C{-}XH_2CH_3$ (X = C, Si, and Ge) and their Cu^+ complexes. Bond lengths in angstroms and bond angles in degrees.

α-carbon is followed by a $C{-}CH_3$ bond cleavage leading to complex **C2**, which lies 23 kcal mol^{-1} above the global minimum.

The third complex of the PES corresponds to the attachment of Cu^+ to the methyl group. It is important to note that for the corresponding Si and Ge containing derivatives a fourth Cu^+-complex, namely **Si4** and **Ge4**, are predicted to be local minima of the potential energy surface. Furthermore, both complexes are estimated to be only 2.2 and 3.3 kcal mol^{-1}, respectively, higher in energy than the corresponding global minima (See Table 1). In this respect, it is important to mention that for the corresponding vinyl compounds, $H_2C{=}C{-}XH_3$ (X = Si and Ge), these relative stabilities were reversed, and the complexes in which the metal cation interacts simultaneously with the π system and with the XH_3 group were predicted to be slightly lower in energy than the conventional π complexes. This can be understood if one takes into account that a $C{\equiv}C$ moiety is more electronegative than a $C{=}C$ one, and therefore the agostic

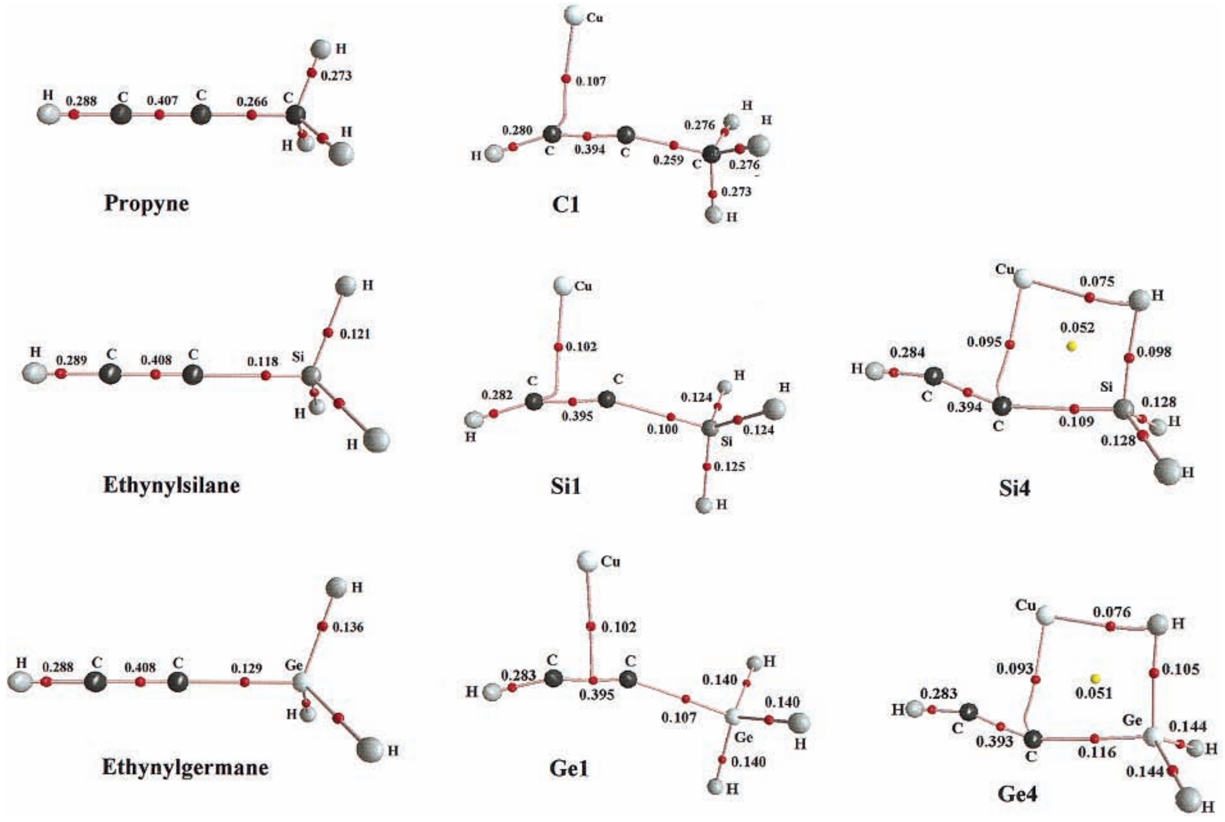


Figure 2. Molecular graphs of the most stable Cu^+ complexes of HC≡C−XH_3 (X = C, Si, and Ge) derivatives showing the bond paths, the position of the bond critical points, ring critical points and the charge density (e au^{-3}) evaluated at these points at the B3LYP/6-311G(d,p) level. The corresponding neutral compounds are included for the sake of comparison.

TABLE 2: Harmonic Vibrational Frequencies[a] (cm^{-1}) of HC≡CXH_3 (X = C, Si, and Ge) Compounds and Their Most Stable Cu^+ Complexes

	HC≡CXH_3										
assignment	X = C	C1	C3	X = Si	Si1	Si3	Si4	X = Ge	Ge1	Ge3	Ge4
CH stretching	3479	3344	3455	3463	3347	3436	3364	3463	3351	3438	3364
XH_3 stretching	3086	3121	3075	2244	2301	2325	2343	2157	2209	2226	2244
	3086	3104	2672[b]	2244	2292	1810[c]	2310	2156	2187	1687[d]	2214
	3027	3036	2640[b]	2243	2272	1776[c]	1729[c]	2156	2173	1648[d]	1571[d]
C−C stretching	2231	2045	2244	2147	1962	2155	1985	2143	1952	2156	1977
C−X stretching	944	910	992	632	571	702	615	510	482	563	523

[a] Calculated at the B3LYP/6-311G(d,p) level. [b] Stretching of the C−H bonds involved in the agostic interaction. [c] Stretching of the Si−H bonds involved in the agostic interaction. [d] Stretching of the Ge−H bonds involved in the agostic interaction.

interaction between the XH_3 group and the metal cation is slightly disfavored in the first case. We will come back to this point later.

In all cases the formation of the π complex leads to a significant lengthening of the C≡C bond. In fact a NBO analysis of the interaction shows the existence of a significant donation from one of the CC π orbitals toward vacant orbitals of Cu^+, and a significant back-donation from lone-pairs of Cu into one of the CC π^* antibonding orbitals. The charge transfer from the CC linkage leads to an enhancement of the electronegativity of the unsaturated moiety which, according to the bond activation rule (BAR) of Alcamí et al.,[41,58] recovers part of this charge by depopulating the C−XH_3 and the C−H bonds, which as a consequence become also longer. These effects are nicely reflected in the charge densities at the C−XH_3 and C−H bond critical points (See Figure 2), which clearly decrease on going from the neutral to the Cu^+ complex, and in significant red shiftings of the corresponding stretching frequencies (See Table 2). It is also worth noting that the effects on the C−XH_3 linkage increase on going from C to Si and Ge, due to the lower electronegativity of the latter two elements.

The interaction of Cu^+ with the XH_3 substituent leads to a significant lengthening of two of the X−H bonds, the third one being practically unaffected. Accordingly, two of the X−H stretching frequencies are significantly shifted to the red. Simultaneously, both the C−X and the C−C bonds become shorter (See Figure 1) and their stretching frequencies appear blue shifted (See Table 2). These effects are quantitatively more important for Si- and Ge-containing systems than those for the corresponding C-containing analogue. These structural changes indicate the existence of an agostic interaction between the metal monocation and the XH_3 substituent. In agreement with the description in ref 30, a NBO analysis of these complexes shows the existence of a stabilizing interaction between two X−H σ bonding MOs and empty orbitals of Cu^+ (dative bond) and a back-donation from filled orbitals of Cu toward the corresponding X−H σ^* antibonding MOs of the base. Coherently, a topological analysis of the charge density shows the existence

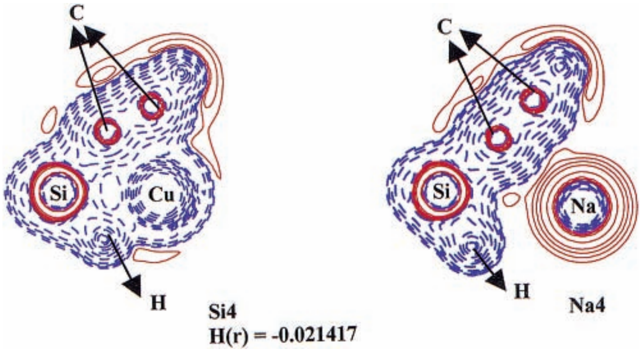


Figure 3. Contour maps of the energy density of Cu^+ and Na^+ complexes of $HC{\equiv}C{-}SiH_3$. Negative values of the energy density are represented by dashed lines, and positive values by solid lines.

TABLE 3: Orbital Interaction Energies (kcal mol^{-1}) Obtained by Means of a Second Order NBO Analysis

complex	$\pi_{CC} \rightarrow$ Cu dative interaction	Cu $\rightarrow \pi_{CC}^*$ back donation	$\sigma_{XH} \rightarrow$ Cu dative interaction	Cu $\rightarrow \sigma_{XH}^*$ back donation
Si4	34.1	16.9	23.3	6.3
MeSi2	32.5	14.8	24.5	6.4
SiMe2	34.3	16.9	27.3	6.8
Ge4	34.1	16.2	26.8	7.4
MeGe2	33.0	14.4	28.1	7.6
GeMe2	35.3	16.3	32.3	8.0

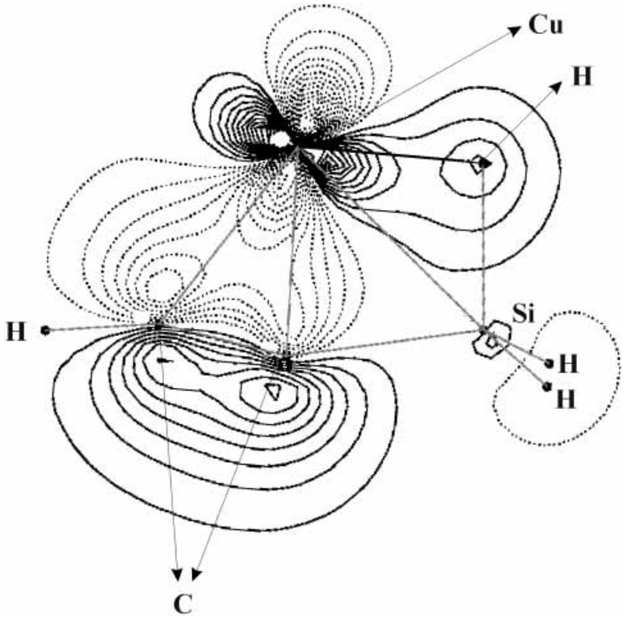
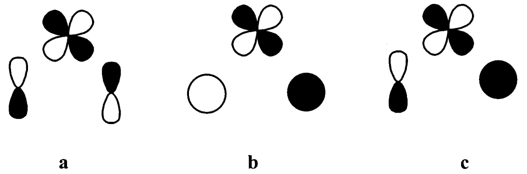


Figure 4. Occupied molecular orbital of the **Si4** complex resulting from in-phase interactions of the d_{z^2} orbital of Cu with the π_{CC} orbital of the neutral and the 1s orbital of one of the hydrogen atoms of the XH_3 group.

SCHEME 1



of bond critical points between Cu and two of the X−H bonds, indicating the existence of a covalent three-center-*n*-electron linkage.

Let us now analyze in detail the bonding in complexes **Si4** and **Ge4**. It can be observed that also in this case there is a lengthening of the C−C bond, although smaller than that found in complexes **Si1** and **Ge1**. Concomitantly there is also a dramatic lengthening of the X−H bond directly interacting with the metal cation, while the other two remain practically unaffected. The bonding pattern corresponds again to a dative bond from the neutral molecule toward the metal and a back-donation from the metal toward antibonding orbitals of the neutral. Indeed, a NBO second order analysis shows that in this case there is a donation not only from one of the π_{CC} bonding orbitals, as in conventional π complexes, but also from one of the Si−H σ bonding orbitals (See Table 3). Consistently the back-donation from filled orbitals of Cu takes place toward the CC π* antibonding and toward the Si−H σ* antibonding orbitals of the base. As expected, these bonding interactions are mirrored in the lengthening of both the CC and the Si−H linkages, and in significant red shiftings of the corresponding stretching frequencies (See Table 2). Table 3 also shows that whereas the $\pi_{CC} \rightarrow$ Cu dative interaction and the Cu $\rightarrow \pi_{CC}^*$ back-donation are almost identical for **Si4** and **Ge4** complexes, the $\sigma_{XH} \rightarrow$ Cu dative interaction is larger for the latter, in agreement with the fact that the binding energies of the germanium derivatives are always slightly larger than those of their Si containing analogues.

Coherently, an analysis of the charge density of these complexes shows that Cu is actually bisligated, forming one bond with C_α and another one with one of the hydrogen atoms of the XH_3 substituent. The formation of this four-membered ring is actually confirmed by the existence of a ring critical point (See Figure 2). Furthermore, the charge densities at these bond critical points are greater than those usually found in typical ionic bonds. This is nicely reflected in the characteristics of the contour map of the energy density (See Figure 3). This magnitude is negative in the bonding regions between Cu and the CC bond of the neutral as well as between Cu and the H of the XH_3 group involved in the agostic interaction, reflecting a nonnegligible covalent character of these linkages. This is more apparent if these maps are compared with those of the complexes involving Na^+, where the interaction is essentially electrostatic. It can be seen that in this latter case the energy density is clearly positive, rather than negative, in the region between the metal cation and the base.

In summary, the bonding in complexes **C1, Si1, Ge1, C3, Si3, Ge3, Si4**, and **Ge4** can be understood again in terms of three-center-n-electron bonds. In the first case the appropriate d orbitals of Cu interact in a bonding manner with the p orbitals of the C═C carbons (See Scheme 1a). In the second kind of complexes this interaction involves the *s* orbitals of the two hydrogen atoms of the XH_3 group (See Scheme 1b). In the third group of complexes the bonding involves a p orbital of C_α and the s orbital of one of the hydrogen atoms of the XH_3 group (See Scheme 1c). Indeed, for instance, an inspection of the occupied molecular orbitals of the **Si4** complex shows the existence of an occupied orbital built up from a bonding interaction between the CC π orbital and the 1s orbital of one of the hydrogens of the SiH_3 group and the d_{z^2} orbital of Cu (See Figure 4).

For propyne any attempt to obtain a complex similar to **Si4** or **Ge4** failed, because these structures collapse to the π complex **C1**. On the other hand, complexes **Si3** or **Ge3** are systematically lower in energy, in relative terms than complex **C3**. Actually while the energy gap between **C1** and **C3** is ca. 31 kcal mol^{-1}, the **Si1**−**Si3** and **Ge1**−**Ge3** energy gaps are 13 and 17 kcal mol^{-1}, respectively. All these findings clearly indicate that the agostic interactions increase down the group, i.e., with the hydride nature of the hydrogen atom which interacts with the metal. This would also explain the lower stability of complexes **Si4** and **Ge4** with respect to similar ones involving the vinyl analogues. The increase of the electronegativity of the unsaturated moiety on going from the vinyl to the ethynyl derivative results in a decrease of the negative charge of the hydrogen atoms of the XH_3 group and, as a consequence, in a less stabilizing agostic interaction. To confirm this argument, we have investigated the effect of substituting either the hydrogen atom of the HC≡C− moiety or one of the hydrogens of the XH_3 group, by a methyl substituent. These Me-substituted derivatives would be identified as Me−X (X = Si and Ge) when the substitution takes place at the carbon atom, and as X−Me (X = Si and Ge) when the substitution takes place at the XH_3 group. Their structures as well as those of the two most stable Cu^+ complexes are also given in Figure 1.

As for the unsubstituted compounds, both the π complexes, namely, **Me−X1** and **X−Me1**, and the agostic one, namely, **Me−X2** and **X−Me2** are also found to be local minima of the PES. More importantly, and in agreement with our expectations, the energy gap between both sets of complexes decreases. When the methyl substituent is attached to C_β both kind of complexes become slightly stabilized, although the effect is slightly larger for the agostic one, due to the expected increase of the hydride character of the XH_3 hydrogen atoms. Interestingly, a second-order NBO analysis indicates that on going from the unsubstituted parent compound to the C-methylated derivative, there is a small decrease of the $\pi_{CC} \rightarrow$ Cu dative and the Cu $\rightarrow \pi_{CC}{}^*$ back-donation interactions, whereas the $\sigma_{XH} \rightarrow$ Cu dative interaction clearly increases (See Table 3). When the hydrogen atom substituted belongs to the XH_3 group, the $\pi_{CC} \rightarrow$ Cu donation remains practically unchanged with regards to the unsubstituted compound, but the $\sigma_{XH} \rightarrow$ Cu dative interaction increases significantly (See Table 3), leading to an enhancement on the stability of the **X−Me2** complexes. As a consequence, the energy gap between **Me−X2** and **X−Me2** complexes becomes almost zero for Si containing derivatives, and only 1.5 kcal mol^{-1} for Ge-containing complexes.

Finally, it would be interesting to compare Cu^+ and H^+ attachment processes. As mentioned in the Introduction, quite often the structure of Cu^+ complexes resembles closely the structure of the corresponding protonated species, the most basic site being the same in protonation and in Cu^+ association reactions. Propyne, ethynylsilane, and ethynylgermane are clear exceptions. In a recent paper,[34] we have shown that these unsaturated compounds protonate preferentially at C_α in a typical dissociative proton attachment process whose product is a tightly bound complex between acetylene and the corresponding $XH_3{}^+$ (X = C, Si, and Ge) cation. Attachment of Cu^+ to C_α also leads to the cleavage of the C_α−XH_3 bond leading to complexes **C2, Si2**, and **Ge2**. However, whereas in the protonated species the $XH_3{}^+$ cation sits above the middle point of the HC≡C moiety for symmetry reasons, in the case of the Cu^+ complexes the $XH_3{}^+$ is bound to the β carbon due to its repulsion with the metal. Also, while protonation at C_α is the most exothermic process, due to the great stability of acetylene molecule, Cu^+ attachment to C_α is not, as a consequence of the relative lower stability of the HC≡CCu moiety formed.

Conclusions

In the interactions between HC≡C(H)XH_3 (X = C, Si, and Ge) compounds with Cu^+ in the gas phase the agostic interactions between the metal cation and the hydrogen atoms of the XH_3 group play an important role. For propyne, however, the interaction with the π-system clearly dominates and the corresponding π-complex, **C1** lies much lower in energy than **C3** in which Cu^+ exhibits an agostic interaction with the methyl group. Since these interactions increase with the hydride character of the hydrogen atoms involved, for ethynylsilane and ethynylgermane, the conventional π complexes, **Si1** and **Ge1**, are only slightly lower in energy than complexes **Si4** and **Ge4**, where Cu^+ interacts simultaneously with C_α and with a hydrogen atom of the XH_3 group. Furthermore, this energy gap is drastically reduced upon methyl substitution of one of the hydrogen atoms of the XH_3 group.

These agostic interactions can be viewed as the result of a donation from a σ_{X-H} (X = C, Si, and Ge) bonding orbital and /or from the π_{CC} bonding orbital of the neutral toward an empty orbital of Cu^+ and a back-donation from filled orbitals of Cu^+ toward a X−H σ^* antibonding orbital and /or toward a CC π^* antibonding orbital of the neutral. As a consequence, a very large weakening of the X−H and /or CC linkages is observed and the corresponding stretching frequencies appear significantly red-shifted. These effects increase down the group reflecting the parallel decrease of the electronegativity of the heteroatom. A topological analysis of the charge density of these complexes seems to be a powerful tool to detect and characterize these agostic bonds, which, consistently with their nonnegligible covalent character, are characterized by negative values of the energy density.

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