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The importance of nonconventional structures in the binding of Ni^+ to ethynylsilanes and ethynylgermanes

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Abstract. The influence of the nature of the heteroatom on the Ni^+ gas-phase binding energies of $HC{\equiv}C{-}XH_3$ (X is C, Si, or Ge) compounds has been investigated through the use of high-level density functional theory methods. The structures of the corresponding Ni^+ complexes were optimized at the B3LYP/6-311G(d,p) level of theory. Final energies were obtained in single-point B3LYP/6-311+G(2df,2p) calculations. Nonconventional π complexes, in which the metal cation interacts simultaneously with the $C{\equiv}C$ π system and with one of the X–H bonds of the substituent XH_3 group, play a significant role in the binding of Ni^+ to $HC \equiv C{-}XH_3$ (X is Si or Ge) derivatives. Conversely, such nonconventional π complexes are not local minima of the propyne–Ni^+ potential-energy surface. This establishes a clear distinction between unsaturated carbon derivatives and the Si- and Ge-containing analogues as far as bonding to transition-metal monocations is concerned. Actually, the attachment of Ni^+ to $HC{\equiv}C{-}XH_3$ (X is Si or Ge) compounds in the gas phase yields a mixture of conventional and nonconventional π complexes. These agostic-type interactions can be viewed as a dative bond from the X–H bonding orbital toward the empty s orbital of the metal, and a back-donation from the valence electron pairs of the metal into the X–H antibonding orbital of the neutral species.

Keywords: Agostic-type interactions – Ni^+ binding energies – Nonconventional π complexes – Ethynylsilanes – Ethynylgermanes

Introduction

In recent papers we have shown that transition-metal monocations, such as Cu^+, interact strongly with $CH_3CH_2XH_3$ saturated and $CH_2{=}CHXH_3$ and $HC{\equiv}C{-}XH_3$ unsaturated silicon- and germanium-containing compounds [1, 2, 3]. For the particular case of saturated compounds, these interactions involve the XH_3 (X is Si or Ge) terminal group to which the metal cation is attached through an agostic-type bond, that can be envisaged as a dative bond from the X–H σ bonding orbital to the empty 4s orbital of the metal, and a back-donation from the valence electron pairs of the metal into the X–H σ* antibonding orbital of the neutral species. For unsaturated compounds, the situation is a little different and the global minimum of the potential-energy surface (PES) corresponds to a nonconventional complex in which the metal monocation interacts with the $C{=}C$ π system and with one of the X–H bonds of the XH_3 terminal group. The most important conclusion of these studies is that the aforementioned agostic-type interactions are particularly strong when involving XH_3 groups associated with electropositive atoms, such as Si and Ge, that favor a significantly high $X^{+\delta}{-}H^{-\delta}$ character of the bonds.

The aim of this paper is to investigate whether similar behavior should be expected for the complexes between the ethynyl derivatives, $HC{\equiv}C{-}XH_3$ (X is C, Si, or Ge) and Ni^+. We also analyze the possible effect of introducing an electron-releasing substituent (CH_3) on the strength of these agostic interactions. A second objective is to investigate whether the fact that Ni^+ is an open-shell system, while Cu^+ is formally a closed-shell monocation, has a significant influence on the corresponding binding energies.

Since clear differences between the intrinsic basicity of Si- and Ge-containing systems and their C-containing

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analogues have already been reported in the literature [4, 5], we have included in this survey the corresponding hydrocarbon analogue, namely propyne, for the sake of comparison. Not much is known, however, on the chemistry [4, 5] of α,β-unsaturated silanes and germanes, among other reasons because some of them are of low stability and their synthesis was described only very recently [6, 7]. Therefore, the present study may contribute to increasing our knowledge of the properties and reactivity of these systems in the gas phase. We hope that the results presented in this paper may guide future experimental studies and that they will provide reliable estimates of the Ni^+ binding energies of these compounds.

Computational details

Standard B3LYP calculations were carried out using the Gaussian98 suite of programs [8]. The B3LYP hybrid density functional method includes Becke's three parameter nonlocal hybrid exchange potential [9] and the nonlocal correlation functional of Lee, Yang, and Parr [10]. The geometries and the harmonic vibrational frequencies of the different species under consideration were optimized by using the all-electron basis of Wachters [11] and Hay [12] (6-311G*) for Ni and the 6-311G(d,p) basis set for the remaining atoms of the system. The corresponding zero-point energies (ZPE) were scaled by the empirical factor 0.9806 [13]. The final energies were obtained in density functional theory B3LYP/6-311+G(2df,2p) single-point calculations using the aforementioned DFT optimized geometries. For Ni the basis set 6-311+G(2df,2p) corresponds actually to the (14s9p5d/9s5p3d) Wachters–Hay [11, 12] basis supplemented with a set of (1s 2p1d) diffuse functions and with two sets of f functions (rather than d) and one set of g functions (rather than f).

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

The intramolecular attractive orbital interactions involved in the agostic bonds were analyzed by means of the natural bond orbital approach [14]. For this purpose, the second-order orbital interaction energies involving occupied orbitals of the neutral species and vacant orbitals of Ni^+, and/or occupied orbitals of Ni^+ and unoccupied antibonding orbitals of the neutral species were evaluated. Alternatively, these agostic-type bonds were also characterized by the values of the charge density at the corresponding bond critical point, in the framework of the atoms in molecules theory [15].

Results and discussion

Structures, relative stabilities

The structures of the different $HC\equiv C–XH_3$ (X is C, Si, or Ge) unsaturated species as well as those of their Ni^+ complexes are given in Fig. 1. Total energies and Ni^+ binding energies are summarized in Table 1. This table

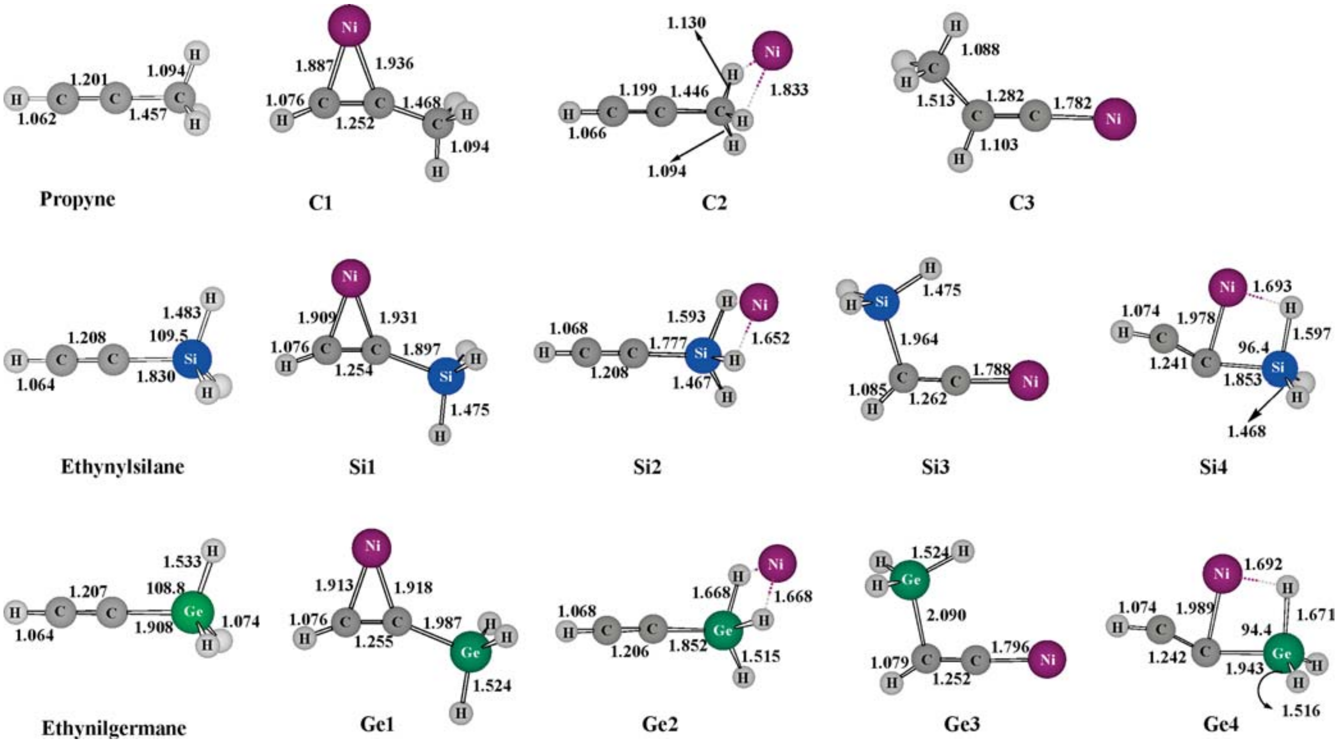

Fig. 1. B3LYP/6-311G(d,p) optimized geometries of $HC\equiv C–XH_3$ (X is C, Si, or Ge) and their Ni^+ complexes. Bond lengths in angstroms and bond angles in degrees

Table 1. Total energies (E, hartrees), zero-point energies (ZPE, hartrees) and Ni^+ binding energies (D_0, kJ mol^{-1}) of $HC \equiv C\ XH_3$, $CH_3C \equiv C\ XH_3$, and $HC \equiv C\ XH_2(CH_3)$ (X is C, Si, or Ge) compounds and their Ni^+ complexes

	$<S^2>$	E^a	ZPE^b	D_0^c
Propyne		−116.7007594	0.055478	
C1	0.757468	−1,624.7459539	0.056470	220.2
C2	0.780118	−1,624.6918804	0.055348	81.2
C3	0.768798	−1,624.7048309	0.056171	113.0
Ethynylsilane		−368.1025600	0.043455	
Si1	0.757735	−1,876.1453479	0.044352	214.2
Si2	0.757358	−1,876.1296779	0.044085	173.7
Si3	0.766897	−1,876.1179478	0.044024	143.1
Si4	0.7556	−1,876.1447126	0.044834	211.3
Ethynylgermane		−2,155.5814300	0.041849	
Ge1	0.757706	−3,663.6290603	0.042533	227.4
Ge2	0.757538	−3,663.6058728	0.042375	167.0
Ge3	0.76728	−3,663.6004985	0.042106	153.5
Ge4	0.755808	−3,663.6252847	0.042618	217.3
Methylderivatives				
Me-Si		−407.4426692	0.071733	
Me-Si1	0.757406	−1,915.4926012	0.072725	232.7
Me-Si2	0.755314	−1,915.4922722	0.072899	231.4
Si-Me		−407.4468623	0.072651	
Si-Me1	0.757506	−1,915.4919762	0.073537	220.3
Si-Me2	0.755777	−1,915.4981986	0.073727	236.2
Me-Ge		−2,194.9208561	0.070066	
Me-Ge1	0.757424	−3,702.9756145	0.070947	245.6
Me-Ge2	0.755465	−3,702.9714974	0.070569	235.8
Ge-Me		−2,194.9212628	0.071060	
Ge-Me1	0.757502	−3,702.9745681	0.071809	242.2
Ge-Me2	0.756019	−3,702.9740556	0.071735	241.0

[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)

also includes the $<S^2>$ values that show that spin contamination of the unrestricted wavefunction is always very small. Only for the less stable complexes of propyne is this contamination slightly higher but it is still not significant.

The propyne–Ni^+ PES presents three local minima, of which the conventional π complex C1 is the global minimum. Attachment to the α-carbon is followed by a C–CH_3 bond cleavage leading to complex C3, which lies 107.2 kJ mol^{-1} above the global minimum. The association of Ni^+ to the terminal methyl group yields the less stable complex C2, 139 kJ mol^{-1} above the global minimum, C1. Conversely, for silicon- and germanium-containing compounds the attachment to the terminal XH_3 (X is Si or Ge) group is much more stabilizing and the corresponding complexes, namely Si2 and Ge2, lie only 40.5 and 60.4 kJ mol^{-1} above the conventional π complexes, Si1 and Ge1, respectively. The most important finding, however, is that for Si and Ge derivatives the nonconventional π complexes (Si4 and Ge4) in which the metal interacts simultaneously with the $C \equiv C$ π system and with one of the X–H bonds are predicted to be local minima of the PES only 2.9 and 10.1 kJ mol^{-1}, respectively, less stable than the global minimum. For the corresponding vinyl compounds, $H_2C{=}C$–XH_3 (X is Si or Ge), similar nonconventional π complexes were found to be the global minimum of the PES [16]. The relative lower stability of the nonconventional π complexes involving $HC \equiv C$–XH_3 compounds simply reflects the higher electronegativity of the $C \equiv C$ group with respect to the $C{=}C$ one. Accordingly, the $X^{+\delta}$–$H^{-\delta}$ polarity of the bonds of the XH_3 attached to it is smaller than in the vinyl derivatives and the corresponding agostic interaction with the metal cation is weaker.

From our calculated free energies, and assuming a Boltzmann distribution, we can estimate that at room temperature 3% of the complexes produced in the gas phase by Ni^+ association to ethynylsilane should correspond to nonconventional π complexes. As we shall see in forthcoming sections, the product distribution changes dramatically upon methyl substitution. As a matter of fact, when the hydrogen atom of the $HC \equiv C$ moiety is substituted by a methyl group the nonconventional complexes are 10.5% of the total. When the substitution takes place at the SiH_3 group the nonconventional π complex becomes dominant, while the conventional one represents only 1.3% of the total.

Bonding

The second-order orbital interaction energies for the different complexes under investigation are presented in Table 2. All the conventional π complexes exhibit quite similar behavior. In all cases there is a dative bond from the C–C triple bond toward an empty orbital of Ni, which is actually an *sd*-type hybrid with dominant participation (95%) of the 4*s* orbital, accompanied by back-donation from valence electron pairs of Ni toward the C–C antibonding orbital. The charge-transfer donation from the C–C π bonding and the population of the C–C π^* antibonding orbital is reflected in a lengthening of the bond, as well as in a decrease of the charge density at the corresponding bond critical point (Fig. 2). Also consistently, the C–C stretching frequency appears redshifted

Table 2. Second-order interaction energies obtained in the natural bond orbital analysis. Orbital interaction energies are given in kilojoules per mole

Complex	Electron-donor interaction		Back-donation	
	Orbitals involved	Second-order energy	Orbitals involved	Second-order energy
C1	$\pi(\mathrm{C_1-C_3}) \rightarrow sd^{*}$ (Ni)	249.0	n_d (Ni) $\rightarrow \pi^{*}(\mathrm{C_1-C_3})$	179.7
C2	$\sigma(\mathrm{C_3-H_5}) \rightarrow sd^{*}$ (Ni)	44.3	n_d (Ni) $\rightarrow \sigma^{*}(\mathrm{C_3-H_5})$	10.0
	$\sigma(\mathrm{C_3-H_6}) \rightarrow sd^{*}$ (Ni)	44.1	n_d (Ni) $\rightarrow \sigma^{*}(\mathrm{C_3-H_6})$	10.2
Si1	$\pi(\mathrm{C_1-C_3}) \rightarrow sd^{*}$ (Ni)	218.2	n_d (Ni) $\rightarrow \pi^{*}(\mathrm{C_1-C_3})$	175.2
Si2	$\sigma(\mathrm{Si_3-H_5}) \rightarrow sd^{*}$ (Ni)	128.8	n_d (Ni) $\rightarrow \sigma^{*}(\mathrm{Si_3-H_5})$	45.4
	$\sigma(\mathrm{Si_3-H_6}) \rightarrow sd^{*}$ (Ni)	128.8	n_d (Ni) $\rightarrow \sigma^{*}(\mathrm{Si_3-H_6})$	45.4
Si4	$\pi(\mathrm{C_1-C_3}) \rightarrow sd^{*}$ (Ni)	176.1	n_d (Ni) $\rightarrow \pi^{*}(\mathrm{C_1-Si_3})$	86.1
	$\sigma(\mathrm{Si_3-H_6}) \rightarrow sd^{*}$ (Ni)	113.3	n_d (Ni) $\rightarrow \sigma^{*}(\mathrm{Si_3-H_6})$	34.7
Ge1	$\pi(\mathrm{C_1-C_3}) \rightarrow sd^{*}$ (Ni)	223.9	n_d (Ni) $\rightarrow \pi^{*}(\mathrm{C_1-C_3})$	175.8
Ge2	$\sigma(\mathrm{Ge_3-H_5}) \rightarrow sd^{*}$ (Ni)	139.2	n_d (Ni) $\rightarrow \sigma^{*}(\mathrm{Ge_3-H_5})$	50.3
	$\sigma(\mathrm{Ge_3-H_6}) \rightarrow sd^{*}$ (Ni)	139.3	n_d (Ni) $\rightarrow \sigma^{*}(\mathrm{Ge_3-H_6})$	50.3
Ge4	$\pi(\mathrm{C_1-C_3}) \rightarrow sd^{*}$ (Ni)	164.8	n_d (Ni) $\rightarrow \pi^{*}(\mathrm{C_1-C_3})$	82.9
	$\sigma(\mathrm{Ge_3-H_6}) \rightarrow sd^{*}$ (Ni)	110.3	n_d (Ni) $\rightarrow \sigma^{*}(\mathrm{Ge_3-H_6})$	40.2
MeSi1	$\pi(\mathrm{C_1-C_3}) \rightarrow sd^{*}$ (Ni)	224.8	n_d (Ni) $\rightarrow \pi^{*}(\mathrm{C_1-C_3})$	166.9
MeSi2	$\pi(\mathrm{C_1-C_3}) \rightarrow sd^{*}$ (Ni)	166.6	n_d (Ni) $\rightarrow \pi^{*}(\mathrm{C_1-C_3})$	77.5
	$\sigma(\mathrm{Si_3-H_6}) \rightarrow sd^{*}$ (Ni)	137.3	n_d (Ni) $\rightarrow \sigma^{*}(\mathrm{Si_3-H_6})$	37.0
SiMe1	$\pi(\mathrm{C_1-C_3}) \rightarrow sd^{*}$ (Ni)	253.5	n_d (Ni) $\rightarrow \pi^{*}(\mathrm{C_1-C_3})$	167.2
SiMe2	$\pi(\mathrm{C_1-C_3}) \rightarrow sd^{*}$ (Ni)	165.2	n_d (Ni) $\rightarrow \pi^{*}(\mathrm{C_1-C_3})$	86.3
	$\sigma(\mathrm{Si_3-H_6}) \rightarrow sd^{*}$ (Ni)	111.1	n_d (Ni) $\rightarrow \sigma^{*}(\mathrm{Si_3-H_6})$	35.6
MeGe1	$\pi(\mathrm{C_1-C_3}) \rightarrow sd^{*}$ (Ni)	231.6	n_d (Ni) $\rightarrow \pi^{*}(\mathrm{C_1-C_3})$	168.9
MeGe2	$\pi(\mathrm{C_1-C_3}) \rightarrow sd^{*}$ (Ni)	156.9	n_d (Ni) $\rightarrow \pi^{*}(\mathrm{C_1-C_3})$	75.5
	$\sigma(\mathrm{Ge_3-H_6}) \rightarrow sd^{*}$ (Ni)	115.7	n_d (Ni) $\rightarrow \sigma^{*}(\mathrm{Ge_3-H_6})$	42.6
GeMe1	$\pi(\mathrm{C_1-C_3}) \rightarrow sd^{*}$ (Ni)	225.1	n_d (Ni) $\rightarrow \pi^{*}(\mathrm{C_1-C_3})$	170.4
GeMe2	$\pi(\mathrm{C_1-C_3}) \rightarrow sd^{*}$ (Ni)	147.9	n_d (Ni) $\rightarrow \pi^{*}(\mathrm{C_1-C_3})$	83.5
	$\sigma(\mathrm{Ge_3-H_6}) \rightarrow sd^{*}$ (Ni)	147.7	n_d (Ni) $\rightarrow \sigma^{*}(\mathrm{Ge_3-H_6})$	41.0

in all cases (Table 3). Another important consequence of the population of the CC antibonding orbital is a change in the hybridization pattern of both carbon atoms that in the complex should not behave as pure *sp* atomic centers. In fact, in the complex the HCC–XH$_3$ moiety is not linear, and both the C–H and the C–X bonds become longer than in the isolated molecule. From a more quantitative point of view, it can be observed that the dative interaction toward the empty orbitals of Ni is slightly stronger for propyne than for the corresponding Si and Ge derivatives. Very likely this is a consequence of a more efficient hyperconjugative interaction between the π system and a methyl group than between the π system and the bulkier XH$_3$ (X is Si or Ge) substituents.

Conversely, the interaction of the metal cation with the terminal XH$_3$ group is significantly stronger for Si and Ge complexes than for the carbon-containing counterpart. In fact, as illustrated in Table 2, the dative bond from the X–H bonding orbitals toward the Ni empty orbitals when X2 complexes are formed, is almost 3 times stronger for HCC–XH$_3$ (X is Si or Ge) than for propyne. Similarly, the back-donation from the valence electron pairs of Ni to the X–H antibonding orbitals in Si and Ge derivatives is also greater than in propyne. Accordingly, the corresponding X–H bonds lengthen, the charge density at the bond critical point decreases, and the stretching frequency appears redshifted.

The nonconventional π complexes, Si4 and Ge4, were only found for Si-and Ge-containing compounds. For these complexes two types of dative bonds can be identified: the one already found in conventional π complexes involving the π_{CC} orbitals, and a second one involving one of the bonds of the XH$_3$ group, similar to those described earlier for the Si2 and Ge2 complexes. Coherently with this picture, the electron density of the Si4 and Ge4 complexes presents a bond critical point between the metal and the substituted carbon of the C≡C moiety, and another one between the metal and one of the hydrogens of the XH$_3$ group. Consistently, there is a lengthening of the X–H bond involved in the agostic interaction, and a significant distortion of the XH$_3$ group. This group in the neutral species has a near-C_{3v} local symmetry, while in the complex it becomes near-C_s, with one of the X–H bonds and the corresponding C–X–H angle is sizably different from the other two (Fig. 1).

Methyl-substituent effects

Taking into account that the stability of the complexes under investigation is closely related to the electron-donor ability of the neutral base, we considered it of interest to investigate the effect that an electron-releasing group, such as the methyl group, may have on the relative stability of conventional and nonconventional π complexes, either when the substituted hydrogen is the one bonded to the C≡C group, or when the substituted hydrogen is one of the hydrogen atoms of the XH$_3$ group. The structures of the neutral compounds and their Ni$^+$ complexes are given in Fig. 3. As could be easily anticipated, methyl substitution at the HC≡C group leads to an enhancement of the stability of the conventional π complex; however, an inspection of the

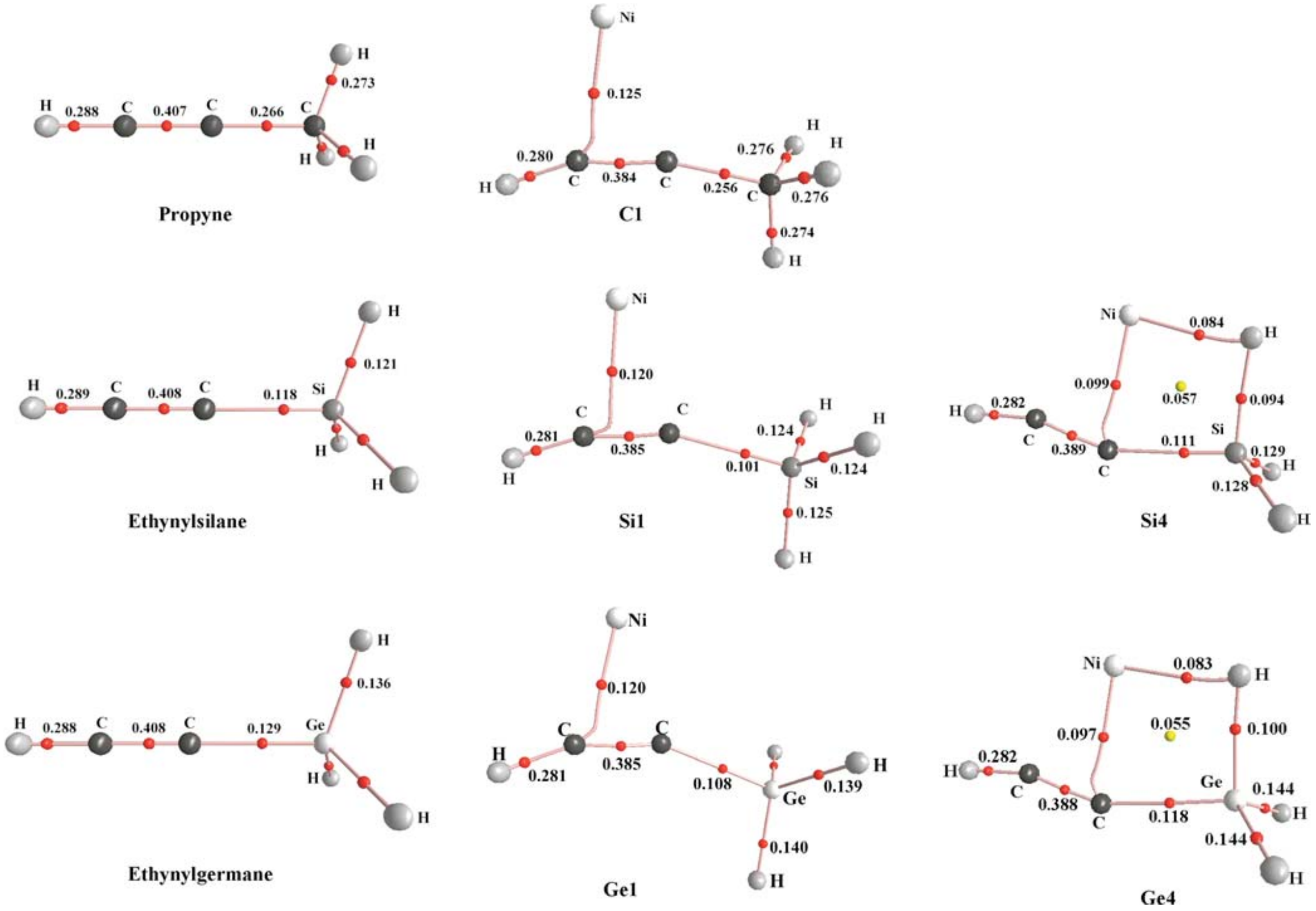

Fig. 2. Molecular graphs of the stablest Ni$^+$ complexes of HC ≡ C–XH$_3$ (X is C, Si, or Ge) derivatives showing the bond paths, the position of the bond critical points, ring critical points and the charge density (e au^{-3}) evaluated at these points at the B3LYP/6-311G(d,p) level. The corresponding neutral compounds are included for the sake of comparison

values of the second-order orbital interaction energies (Table 2) shows only a very small increase in the C–C → Lp*(Ni) interaction upon methyl substitution. This seems to indicate that a significant part of the stability enhancement of the complex must be associated with the increase of the polarizability of the base. As far as the nonconventional π complex is concerned, there is a nonnegligible increase in the energy associated with the XH → Lp*(Ni) dative interactions, but a concomitant decrease of the C–C → Lp*(Ni), so both effects nearly cancel each other. Hence, in this case the basicity enhancement can also be associated with the increase of the polarizability of the system. As a consequence, the energy gap between conventional and nonconventional π complexes does not change significantly upon methyl substitution of the HC≡C hydrogen.

At variance with this, the substitution of a hydrogen atom of the SiH$_3$ group by a methyl group clearly enhances the donor ability of the Si–H bonds, favoring the nonconventional π complex that becomes 15.9 kJ mol^{-1} lower in energy than the conventional one. The situation is rather similar when substitution takes place at the

Table 3. Harmonic vibrational frequencies (cm^{-1}) calculated at B3-LYP/6-311G(d,p) level of HC ≡ C XH$_3$ ($X$is C, Si, or Ge) compounds and their stablest Ni$^+$ complexes

HC ≡ C XH$_3$											
Assignment	$X=$C	C1	C2	$X=$Si	Si1	Si2	Si4	$X=$Ge	Ge1	Ge2	Ge4
CH stretching	3,479	3,314	3,455	3,463	3,313	3,434	3,343	3,463	3,315	3,436	3,341
XH$_3$ stretching	3,086	3,119	3,076[a]	2,244	2,299	2,324[a]	2,343[a]	2,157	2,203	2,222[a]	2,241[a]
	3,086	3,111	2,675	2,244	2,290	1,677	2,311[a]	2,156	2,194	1,557	2,213[a]
	3,027	3,040	2,638	2,243	2,271	1,348	1,632	2,156	2,177	1,186	1,481
C–C stretching	2,231	1,946	2,243	2,147	1,880	2,151	1,941	2,143	1,868	2,152	1,927
C–X stretching	944	905	995	632	592	708	631	510	521	570	529

[a] Stretching of the X–H bonds not involved in the agostic interactions

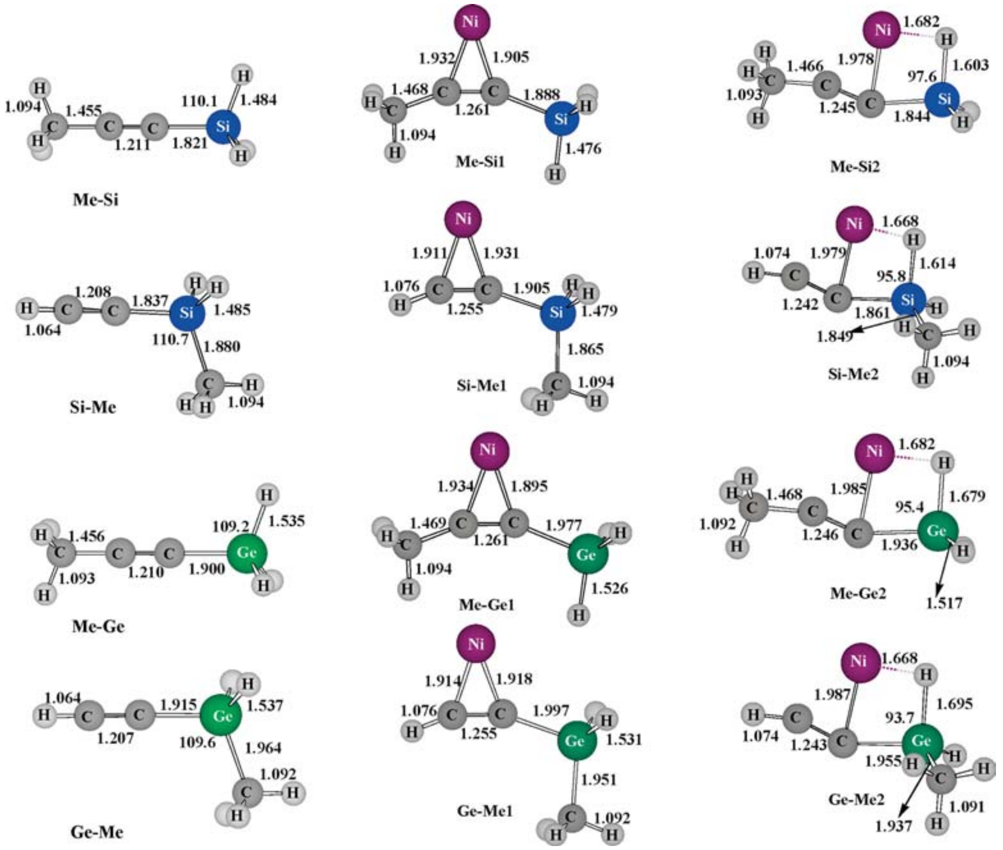

Fig. 3. B3LYP/6-311G(d,p) optimized geometries of CH_3-C ≡ C–$X$$H_3$ and H–C ≡ C–$X$$H_2CH_3$ (X is Si or Ge) and their Ni^+ complexes. Bond lengths in angstroms and bond angles in degrees

GeH_3 group to yield Ge-Me2, although in this case, owing to the smaller electronegativity of Ge, the nonconventional π complex, although clearly stabilized, is predicted to lie 1.2 kJ mol^{-1} higher still in energy than the conventional one.

Ni^+ versus Cu^+ binding energies

A comparison between Ni^+ and the Cu^+ binding energies taken from Ref. [3] for the same set of compounds (Table 1) reveals that HC ≡ C–XH_3 (X is C, Si, or Ge) compounds bind Ni^+ more strongly than Cu^+. The fact that the agostic interactions of Ni^+ with the X–H bonds are stronger than those involving Cu^+ is reflected in the values of $\rho(\mathbf{r})$ at the metal–H bond critical points. For example, the charge densities at the Ni–H bond critical points in complexes Si4 and Ge4 are systematically larger (0.084 and 0.083 e au^{-3}, respectively) than those obtained [3] for the corresponding Cu–H linkages (0.075 and 0.076 e au^{-3}, respectively). Also, the lengthening of the X–H bonds (0.114 and 0.138 Å, respectively) is greater upon Ni^+ attachment than upon Cu^+ association (0.094 and 0.116 Å, respectively). Similarly, the redshifting of the corresponding stretching frequencies (1,632 and 1,481 cm^{-1}) is also significantly larger for Ni^+ complexes (655 and 612 cm^{-1}) than for the corresponding Cu^+ complexes (514 and 585 cm^{-1}) [3].

These differences can be understood if one takes into account that while Cu^+ is formally a closed-shell system, with all its d orbitals occupied, Ni^+ is an open-shell cation, with a vacancy in one of the d orbitals, and therefore it must behave as a better electron acceptor. On the other hand, Cu^+, as a closed-shell system, must be a poorer electron donor, as reflected in a higher ionization potential, and its n_d electron pair should be less diffuse than that of Ni^+. It is also worth noting that, as shown in Fig. 4, there is a quite good linear correlation between both Ni^+ and Cu^+ binding energies.

Conclusions

We have shown that nonconventional π complexes, in which the metal cation interacts simultaneously with the C ≡ C π system and with one of the X–H bonds of the substituent XH_3 group, may play a significant role in the binding of Ni^+ to HC ≡ C–XH_3 (X is Si or Ge) derivatives. Conversely, such nonconventional π complexes are not local minima of the propyne–Ni^+ PES. This establishes a clear distinction between carbon derivatives and the analogues containing Si and Ge as far as bonding to transition-metal monocations is concerned. The fact that for Si and Ge derivatives the X–H bonds have a clear $X^{+\delta}$–$H^{-\delta}$ polarity favors agostic-type interactions between these groups and the metal, through a dative bond from the X–H bonding orbital

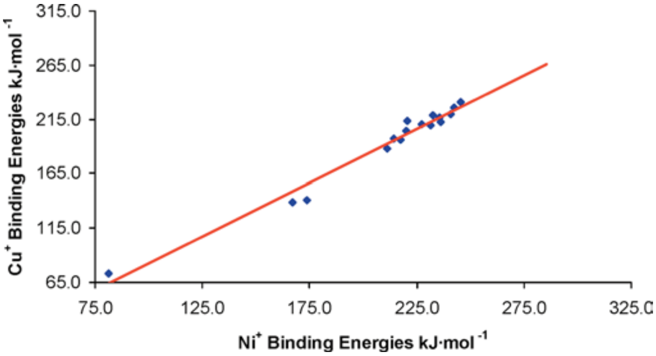

Fig. 4. Linear correlation between Ni^+ and Cu^+ binding energies (*BEs*) of $HC \equiv C{-}XH_3$ (X is C, Si, or Ge), $CH_3{-}C \equiv C{-}XH_3$ and the $H{-}C \equiv C{-}XH_2CH_3$ (X is Si or Ge) derivatives. Least-squares regression fulfils the equation $Cu^+(BE) = 0.9872 \times Ni^+(BE) - 16.016$ ($r^2 = 0.9737$)

toward the empty *s* orbital of the metal, and a back-donation from the valence electron pairs of the metal into the X–H antibonding orbital of the neutral species.

As a consequence, a very large weakening of the X–H bonds is observed and the corresponding stretching frequencies appear significantly redshifted. A topological analysis of the charge density of these complexes seems to be a powerful tool to detect and characterize these agostic bonds.

The main conclusion of this analysis is that in the gas phase the association of Ni^+ to $HC \equiv C{-}XH_3$ (X is Si or Ge) compounds should yield a mixture of conventional and nonconventional π complexes.

There is a good linear correlation between Ni^+ and Cu^+ binding energies, although the former are systematically greater than the latter.

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