

# On the stability of non-conventional $\pi$ -complexes between $\text{Ni}^+$ and toluene, phenyl-silane and phenyl-germane<sup>†</sup>

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**ABSTRACT:** The complexes between  $\text{Ni}^+$  and toluene, phenylsilane, and phenylgermane were investigated through the use of high-level density functional theory (DFT) methods. Both harmonic vibrational frequencies and optimized geometries were obtained at the B3LYP/6-311G(d,p) and B3LYP/6-311+G(2df,2p) levels of theory. These results show that at the highest level considered in this work, and in contrast with what was found before for  $\text{Cu}^+$ , the complexes in which  $\text{Ni}^+$  interacts specifically with only one pair of carbon atoms of the aromatic ring collapse to the conventional  $\pi$ -complexes. However, similarly to  $\text{Cu}^+$ , non-conventional complex in which the metal ion interacts with the *ortho* carbon of the aromatic ring and with one of the hydrogen atoms of the  $\text{XH}_3$  ( $\text{X} = \text{Si}, \text{Ge}$ ) substituent group, through a typical agostic-type interaction are very stable. Nevertheless, whereas for  $\text{Cu}^+$  these agostic-type complexes are not only the global minima of the potential energy surface but the dominant species in the gas phase, for  $\text{Ni}^+$  they are slightly less stable than the conventional  $\pi$ -complexes. Agostic-type complexes exhibit infrared spectra that are markedly different from those of the conventional  $\pi$ -complexes, and therefore they could be easily identified using this spectroscopic technique. Copyright © 2006 John Wiley & Sons, Ltd.

**KEYWORDS:** toluene; phenyl-silane; phenyl-germane;  $\text{Ni}^+$  complexes; non-conventional complexes; theoretical calculations

## INTRODUCTION

The interactions between transition metal ions and organic compounds have attracted much attention<sup>1–8</sup> because its knowledge is important to understand, at the molecular level, the mechanisms of many interesting reactions, including catalytic and biochemical processes. We have paid particular attention in recent years to the interaction of transition metal monocations with  $\alpha, \beta$ -unsaturated compounds, containing different kind of heteroatoms, such as phosphorus, arsenic, silicon or germane.<sup>9–12</sup> These studies showed that silanes and germanes derivatives exhibit enhanced  $\text{Cu}^+$ - and  $\text{Ni}^+$ -binding energies with respect to the corresponding carbon analogs<sup>13</sup> because in the former the formation of agostic-type interactions between the  $\text{SiH}_3$  and  $\text{GeH}_3$  groups and the transition metal monocation,<sup>14</sup> are favored. These agostic-type linkages are the result of an electron donation from the  $\sigma_{\text{X-H}}$  ( $\text{X} = \text{Si}, \text{Ge}$ ) bonding orbitals of the base toward the 4s empty

orbital of the metal cation, and a back donation from d occupied orbitals of the metal toward the corresponding  $\sigma_{\text{X-H}}^*$  antibonding orbitals of the base.<sup>15,16</sup> This mechanism is significantly favored when the bonds of the neutral base exhibit a  $\text{X}^{+\delta}-\text{H}^{-\delta}$  polarity, and therefore agostic-type interactions are stronger in Si and Ge-containing compounds than in the corresponding hydrocarbons. Also coherently, their strength decreases on going from vinyl to ethynyl derivatives,<sup>12</sup> because the  $-\text{C}=\text{C}$  group is less electronegative than the  $-\text{C}\equiv\text{C}$  one. More recently, we have shown that the same type of bonding is responsible for the enhanced  $\text{Cu}^+$  binding energies of phenylsilane and phenylgermane with respect to toluene.<sup>17</sup> The aim of this paper is to investigate whether a similar situation is found when  $\text{Cu}^+$ , which is a closed-shell  $d^{10}$  monocation, is replaced by  $\text{Ni}^+$ , which is a  $d^9$  open-shell system. We aim also at analyzing whether, as in the case of  $\text{Cu}^+$ , the non-conventional agostic-type complexes present a force field markedly different from the conventional  $\pi$ -systems due to the large red-shifting of the X-H stretching displacement, associated with the depopulation of the  $\sigma_{\text{X-H}}$  bonding orbital, and the simultaneous population of the  $\sigma_{\text{X-H}}^*$  antibonding of the X—H bond which participates in the agostic interaction. Toluene was included in this survey to have as a reference a system in which the agostic interactions are rather weak.

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Stepnowski and Allison<sup>18</sup> were the first to study experimentally the gas-phase chemistry of Ni<sup>+</sup> with a series of aromatic compounds by means of Ion Cyclotron mass spectrometry techniques. The reaction products observed for these reactions are NiC<sub>6</sub>H<sub>4</sub><sup>+</sup>, NiC<sub>5</sub>H<sub>5</sub><sup>+</sup> and C<sub>7</sub>H<sub>7</sub><sup>+</sup>, the latter resulting from a charge transfer process. In the case of benzene and toluene, however, no reaction was observed. This was attributed by the authors either to the endothermicity of the overall reaction or to a not favorable initial insertion of the metal into the C—X bond.

## COMPUTATIONAL DETAILS

The geometries of the different Ph-XH<sub>3</sub>-Ni<sup>+</sup> (X = C, Si, Ge) complexes were initially optimized using the B3LYP density functional theory (DFT) approach together with a 6-311G(d,p) basis set expansion. Harmonic vibrational frequencies were obtained at the same level of theory to classify the stationary points as local minima or transition states and to estimate the corresponding zero point energies (ZPE), which were scaled by the empirical factor 0.9806.<sup>19</sup> It is nowadays well established<sup>20,21</sup> that the use of B3LYP geometries and harmonic frequencies leads to an improvement of the agreement between calculated and experimental thermochemical data. This functional includes Becke's three parameter non-local hybrid exchange potential<sup>22</sup> and the non-local correlation functional of Lee, Yang, and Parr.<sup>23</sup>

Once the different local minima were located on the potential energy surface at the B3LYP/6-311G(d,p) level, their geometries were refined at the B3LYP/6-311+G(2df,2p) level, that includes diffuse functions on all heavy atoms, as well as high angular momentum functions, that may be important when describing  $\pi$ -complexes. For Ni the 6-311+G(2df,2p) basis set corresponds actually to the (14s9p5d/9s5p3d) Wachters-Hay<sup>24,25</sup> 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*). Calculation of harmonic vibrational frequencies at this latter level of theory allowed us to assess which local minima remain as such when the larger basis set expansion is used.

Ni<sup>+</sup> binding enthalpies, BE's, were evaluated by subtracting from the B3LYP energy of the complex the energy of the neutral and that of the metal cation, after including the corresponding B3LYP thermal corrections.

All these calculations have been carried out by using the Gaussian-98 suite of programs.<sup>26</sup>

In order to characterize the possible agostic-type interactions between the phenyl derivatives and Ni<sup>+</sup>, we have employed the second order perturbation NBO analysis,<sup>27</sup> which permits to identify and quantify the interactions between occupied orbitals of the neutral and the vacant orbitals of Ni<sup>+</sup>, and/or between the *d* occupied

orbitals of Ni<sup>+</sup> and the empty antibonding orbitals of the base. At the same time, complementary information on the strength of these covalent interactions was obtained by locating the corresponding bond critical points (bcps), within the framework of the atoms in molecules (AIM) theory.<sup>28</sup> The calculated electron density at these bcps, is a good measure of the strength of the linkage. The covalent nature of the interaction will be characterized by means of the contour maps of the energy density, defined as:

$$H(\vec{r}) = \frac{1}{4}\nabla^2\rho(\vec{r}) - G(\vec{r})$$

where  $\nabla^2\rho(\vec{r})$  and  $G(\vec{r})$  are the laplacian of the electron density and the kinetic energy density, respectively. Bonding regions in which the energy density is negative correspond to covalent linkages.<sup>12,29</sup> Conversely, typical ionic bonds are associated with regions where the energy density is clearly positive.

## RESULTS AND DISCUSSION

### Structures and relative stabilities

The total energies, entropies, relative enthalpies, relative free energies, and the corresponding binding energies are summarized in Table 1. This table includes also the total spin  $\langle S^2 \rangle$  expectation values to show that in any of the systems investigated the spin contamination was significant, as in all cases this value is close to that corresponding to pure doublets (0.75). From our previous study on similar Cu<sup>+</sup>-complexes, one would expect that besides the conventional  $\pi$ -complex **X1** (X = C, Si, Ge), in which the metal cation, M<sup>+</sup>, is located above the aromatic ring (scheme 1) other three types of complexes, namely **X2**, **X3**, **X4** (X = C, Si, Ge) (scheme 1), in which M<sup>+</sup> interacts with the *ipso* and *ortho*, the *ortho* and *meta* and the *meta* and *para* carbon atoms, would be also local minima of the PES. However, there are significant dissimilarities between Cu<sup>+</sup> and Ni<sup>+</sup> that deserve to be commented.

All **X1**–**X4** structures for phenylsilane- and phenylgermane-Cu<sup>+</sup> complexes were found to be local minima of the PES at the B3LYP/6-311G(d,p) level, but when this metal cation is replaced by Ni<sup>+</sup>, only **X1** and **X4** for the case of phenylsilane and **X1**, **X2**, and **X4** for the case of phenylgermane remain as local minima of the corresponding PES's, because the other structures evolve to yield the conventional  $\pi$ -complex, **X1**. However, the most important differences are found when looking at the relative energies. In toluene-Cu<sup>+</sup> complexes, the global minimum of the PES corresponded to complex **C4**, which was predicted<sup>17</sup> to be 8.2 kJ mol<sup>-1</sup> more stable than the conventional  $\pi$ -complex, **C1**, at the same level of theory. For toluene-Ni<sup>+</sup> complexes, not only the global minimum is the conventional  $\pi$ -complex, but the energy gap of complexes **C2** and **C4** with respect to **C1** is very

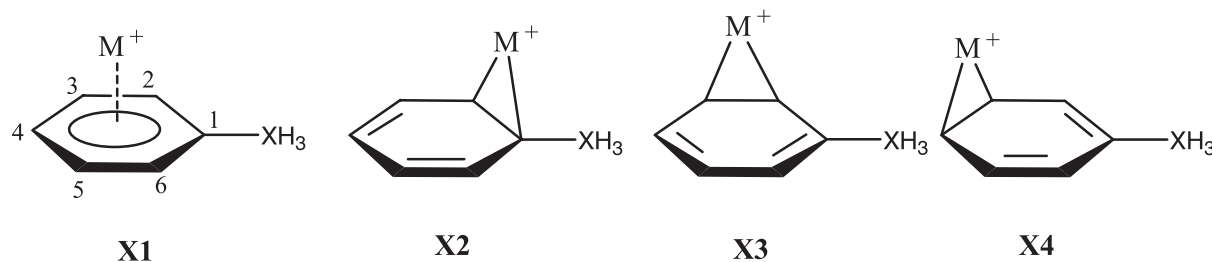
**Table 1.** Total energies ( $E$ , hartrees), entropies ( $S$ , cal mol<sup>-1</sup> K<sup>-1</sup>), relative enthalpies ( $\Delta H$  kJ mol<sup>-1</sup>), relative free energies ( $\Delta G$ , kJ mol<sup>-1</sup>), and binding energies<sup>a</sup> ( $D_0$ , kJ mol<sup>-1</sup>)

System	B3LYP/6-311G(d,p)					B3LYP/6-311 + G(2df,2p)						
	$E$	$\langle S^2 \rangle$	$\Delta H$	$\Delta G$	$D_0$	$E$	$\langle S^2 \rangle$	$S$	$\Delta H$	$\Delta G$	$D_0$	
Ph-CH <sub>3</sub>	-271.63605					-271.65706		80.768				
<b>C1</b>	-1779.64632	0.756	<b>0.0</b>	<b>0.0</b>	305.0	-1779.71599	0.755	89.599	<b>0.0</b>	<b>0.0</b>	256.0	
<b>C2</b>	-1779.62681	0.754	52.5	51.1	252.4	—	—	—	—	—	—	
<b>C3</b>	-1779.63378	0.761	34.3	30.2	271.1	—	—	—	—	—	—	
<b>C4</b>	-1779.63417	0.762	33.2	29.6	272.0	—	—	—	—	—	—	
Ph-SiH <sub>3</sub>	-523.02725					-523.04942		85.414				
<b>Si1</b>	-2031.03487	0.756	0.5	<b>0.0</b>	298.2	-2031.10430	0.755	95.290	0.2	<b>0.0</b>	246.0	
<b>Si2</b>	—	—	—	—	—	—	—	—	—	—	—	
<b>Si3</b>	—	—	—	—	—	—	—	—	—	—	—	
<b>Si4</b>	-2031.02055	0.761	39.1	34.9	259.9	—	—	—	—	—	—	
<b>Si5</b>	-2031.03595	0.757	<b>0.0</b>	3.5	297.1	-2031.10445	0.755	92.789	<b>0.0</b>	2.9	244.9	
<b>Si6</b>	-2031.01627	0.758	51.1	49.6	246.3	-2031.09284	0.755	95.199	29.7	29.6	215.2	
Ph-GeH <sub>3</sub>	-2310.51282					-2310.53145		86.048				
<b>Ge1</b>	-3818.52150	0.756	4.7	0.6	301.7	-3818.58768	0.755	98.704	<b>0.0</b>	<b>0.0</b>	250.1	
<b>Ge2</b>	-3818.50990	0.762	36.4	27.9	270.4	—	—	—	—	—	—	
<b>Ge3</b>	—	—	—	—	—	—	—	—	—	—	—	
<b>Ge4</b>	-3818.50704	0.761	43.9	37.3	262.5	—	—	—	—	—	—	
<b>Ge5</b>	-3818.52385	0.757	<b>0.0</b>	<b>0.0</b>	304.8	-3818.58726	0.755	95.816	0.8	4.4	247.9	
<b>Ge6</b>	-3818.50337	0.758	52.1	46.3	253.4	-3818.57462	0.755	98.932	32.5	32.3	216.4	
Ni <sup>+</sup>	-1507.89375	0.750				-1507.96033						

<sup>a</sup> Binding energies include scaled ZPE corrections.

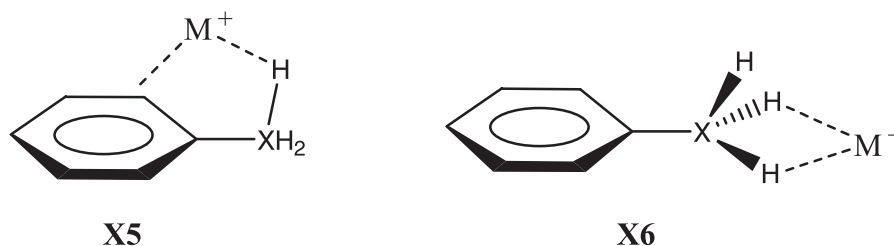
large (51.1 and 29.6 kJ mol<sup>-1</sup>, respectively, Table 1). Something similar can be said as far as phenylsilane and phenylgermane are concerned. When the reference acid was Cu<sup>+</sup>, it was found that complexes **X1–X4** were very close in energy, all of them within an energy gap of *ca.* 10 kJ mol<sup>-1</sup>, at the same level of theory. Conversely, when the attacking ion is Ni<sup>+</sup>, the conventional  $\pi$ -complexes,

**Si1** and **Ge1**, are systematically favored with respect to **X2–X4** complexes. This enhanced stability of the conventional  $\pi$ -complexes is likely behind the fact that when the basis set expansion is enlarged from 6-311G(d,p) to 6-311 + G(2df,2p) any of the **X2–X4** structures remain as local minima of the PES since all of them collapse to the conventional  $\pi$ -complex, **X1**,



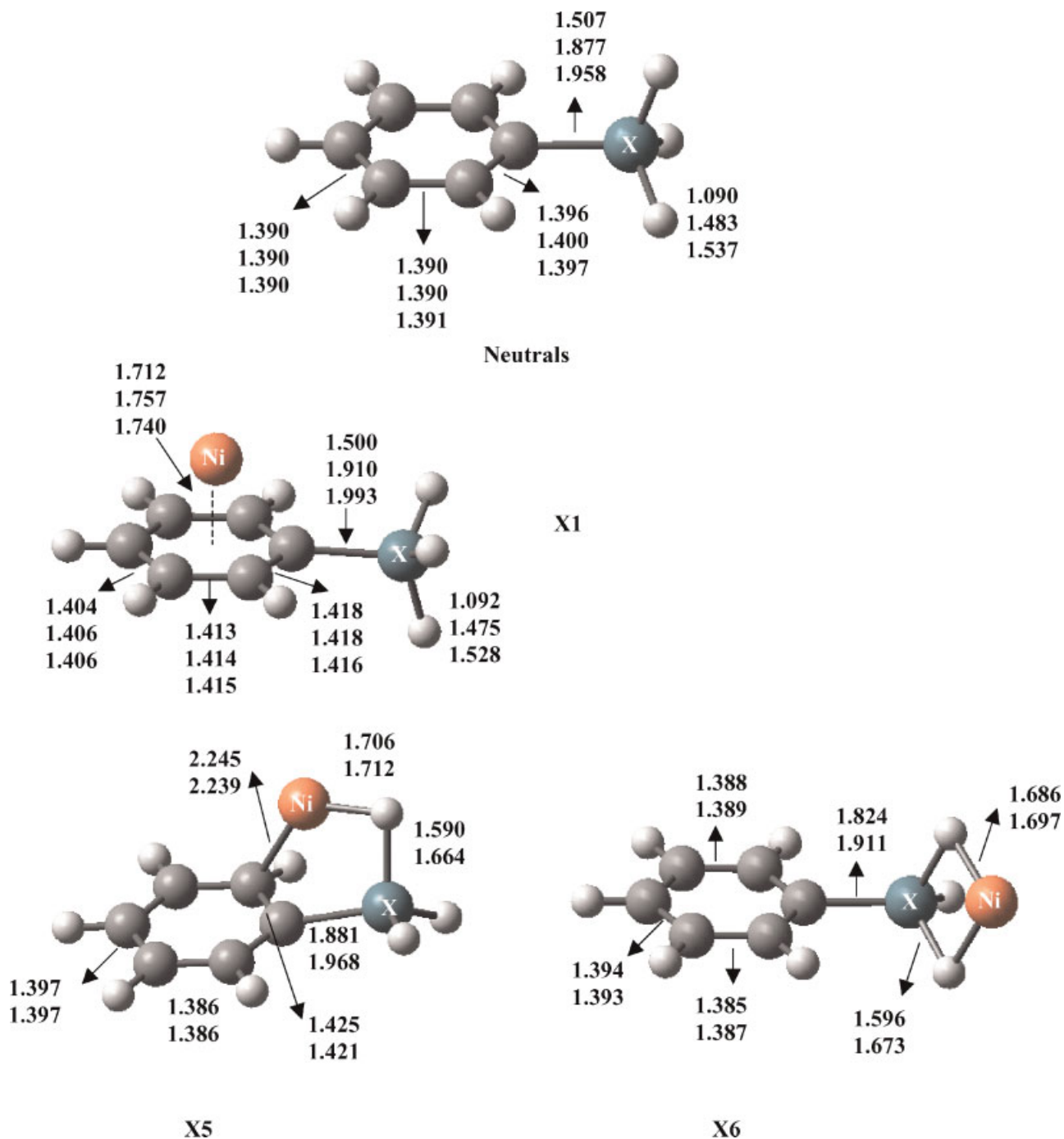
**X = C, Si, Ge ; M = Cu, Ni**

**Scheme 1**



**X = Si, Ge ; M = Cu, Ni**

**Scheme 2**



**Figure 1.** B3LYP/6-311 + G(2df,2p) optimized geometries for Ph-XH<sub>3</sub> (X = C, Si, Ge) derivatives and their Ni<sup>+</sup> complexes. The first value corresponds to X = C, the second to X = Si, and the third to X = Ge. **X5**- and **X6**-type complexes do not exist when X = C. All values are in Å [This figure is available in colour online at [www.interscience.wiley.com](http://www.interscience.wiley.com)]

what denotes the incompleteness of the smaller basis set. One should expect, however, the larger basis set expansion to be suitable for the description of these systems, as it contains high angular polarization functions as well as diffuse functions. As a matter of fact, it has been shown to yield quite accurate Cu<sup>+</sup> and Li<sup>+</sup> binding energies.<sup>30–32</sup>

It is important to stress that this finding is of some relevance because most of the theoretical models are based on single-point calculations with a large basis set

expansion on optimized geometries obtained with a smaller basis set. It is quite obvious that this model would not be reliable in the present case, where some of the stationary points found at the lower level disappear when the geometry is refined at a higher level.

In coincidence, however, with what was found before for Cu<sup>+</sup>-interactions, phenylsilane and phenylgermane, lead to very stable agostic-type complexes **X5** (X = Si, Ge) (scheme 2), in which the metal interacts simultaneously with one of the hydrogen atoms of the XH<sub>3</sub>

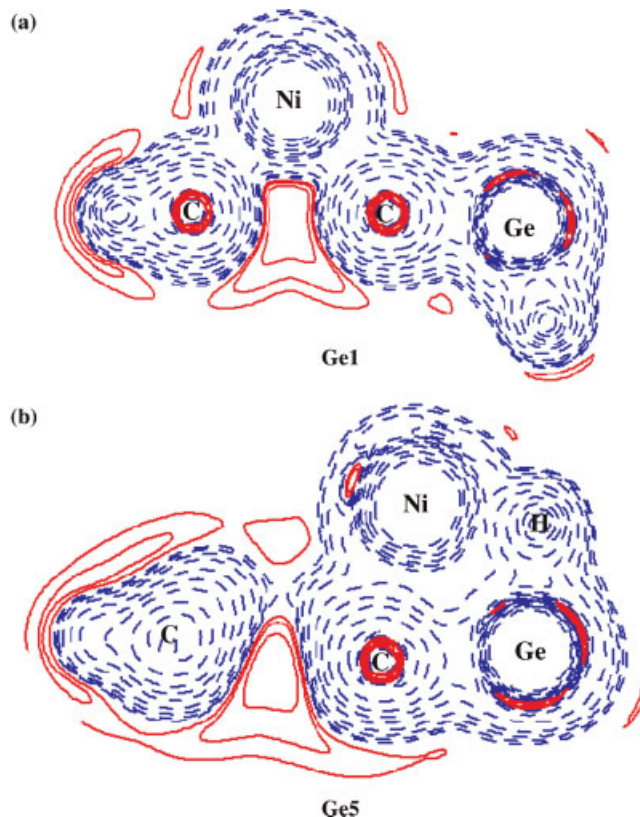
substituent and with the *ortho* carbon atom of the aromatic moiety. For toluene, as it has been found before for the corresponding  $\text{Cu}^+$  complexes,<sup>17</sup> this structure is not a stationary point of the PES, as it collapses to yield **C1**. The less favorable association corresponds systematically to that in which the metal cation interacts with two hydrogen atoms of the substituent (complexes **X6**, scheme 2). This kind of complexes does not exist when the substituent is a methyl group, again in line with what was found for the corresponding  $\text{Cu}^+$ -complexes.<sup>17</sup>

However, once more there are significant dissimilarities between  $\text{Ni}^+$  and  $\text{Cu}^+$  from the quantitative point of view. For  $\text{Cu}^+$  the **X5**-type complexes are clearly the dominant species, since they are predicted to be about  $7 \text{ kJ mol}^{-1}$  lower in energy than the  $\pi$ -conventional complexes.<sup>17</sup> These calculated energy gaps reduce to  $0.2 \text{ kJ mol}^{-1}$  for phenylsilane and changes sign ( $-0.8 \text{ kJ mol}^{-1}$ ) for phenylgermane in the case of complexes with  $\text{Ni}^+$  (Table 1). Besides, it must be taken into account that, in general, the agostic-type complexes, **X5**, are entropically disfavored (Table 1), and as a consequence, when the relative stabilities are analyzed in terms of free energies, which are the ones that matter to establish in which proportion the different species will be found in the gas phase, one finds that the stability order is also reversed for phenylsilane. However, both relative **X1–X5** enthalpies and free energies values lie within the error inherent to the theoretical method used in this study and therefore apart from the fact that both structures have a similar stability it would not be possible to establish which of the two species, the conventional  $\pi$  complex or the agostic complex, would be the dominant in the gas-phase. Moreover, the height of the barrier between both structures would be an additional factor to establish whether both isomers will be experimentally accessible.

The structures of the stable complexes of toluene, phenylsilane and phenylgermane with  $\text{Ni}^+$  are presented in Figure 1.

## Bonding characteristics

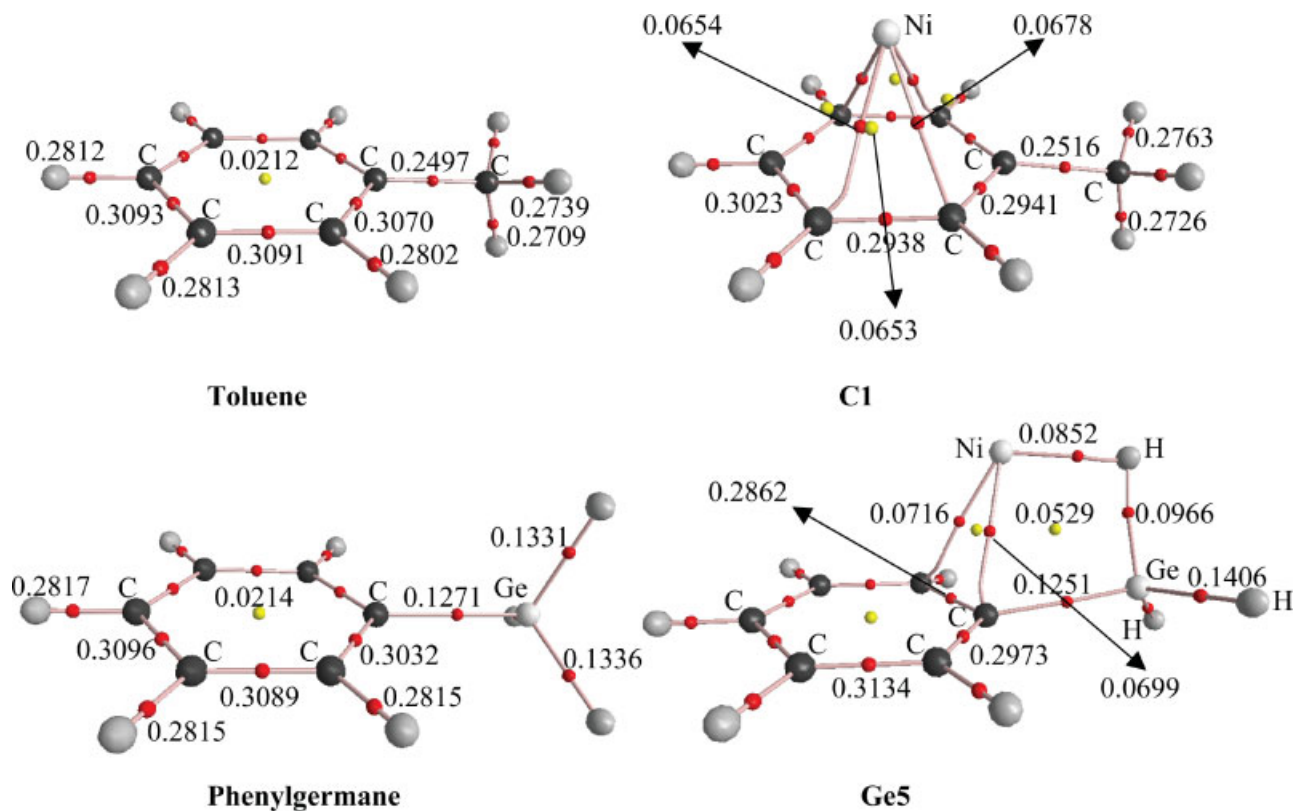
It is useful, in order to analyze the bonding in these complexes to examine the characteristics of the contour maps of the energy density,  $H(\mathbf{r})$ . These maps are shown in Figure 2 for the particular cases of the conventional  $\pi$ - and the agostic-type structures of phenylgermane- $\text{Ni}^+$  systems. It is well established that the interactions between transition metal cations and neutral bases is dominantly electrostatic, as it is also the case for the interactions with alkali metal cations. However, while the former have a non-negligible covalent component, this is completely absent in the latter. In fact, as shown in Figure 2, the energy density between  $\text{Ni}^+$  and the base is negative, indicating that there is a dominant weight of the potential energy component over the kinetic energy one, typical of covalent linkages. This covalent nature has its origin in the



**Figure 2.** Energy density contour maps for (a) **Ge1** complex, (b) **Ge5** complex. In (a) the energy density is plotted in a plane perpendicular to the aromatic ring and containing the substituted and the *para* carbon atoms. In (b) the energy density has been plotted in the plane that contains the Ge–H bond of the substituent and the substituted carbon atom [This figure is available in colour online at [www.interscience.wiley.com](http://www.interscience.wiley.com)]

donations and back-donations that take place between the occupied and the empty orbitals of both interacting subunits (base and metal cation) that cannot occur when the ion is an alkali metal. An inspection of the NBO second order energy interactions in **Ge1** clearly shows that there is a donation from the C–C  $\pi$ -bonding orbitals of the base towards the empty 4s orbital of the metal, and a back-donation from the occupied d orbitals of the metal into the C–C  $\pi^*$ -antibonding orbitals of the base. Consistently, the depopulation of the C–C  $\pi$ -bonding orbitals and the concomitant population of the C–C  $\pi^*$ -antibonding orbitals leads to a decrease in the charge density at the corresponding bcps (Figure 3). Consistently, a lengthening of the C–C bonds in complex **Ge1** with respect to the isolated base, of the order of  $0.019 \text{ \AA}$  in average (Figure 1), and a red-shifting of *ca.*  $80 \text{ cm}^{-1}$  of the corresponding stretching frequencies, are observed.

In complex **Ge5**, the donation from the base to the 4s empty orbital of the metal takes place from one of the  $\sigma_{\text{Ge-H}}$  bonding orbitals as well as from the C1–C2 bonding  $\pi$ -orbital, while the back-donation from the filled d orbitals of the metal involves the corresponding  $\sigma_{\text{Ge-H}}^*$  and  $\pi_{\text{C1-C2}}^*$  antibonding orbitals. The significant depopulation of the  $\sigma_{\text{Ge-H}}$  bonding together with the population



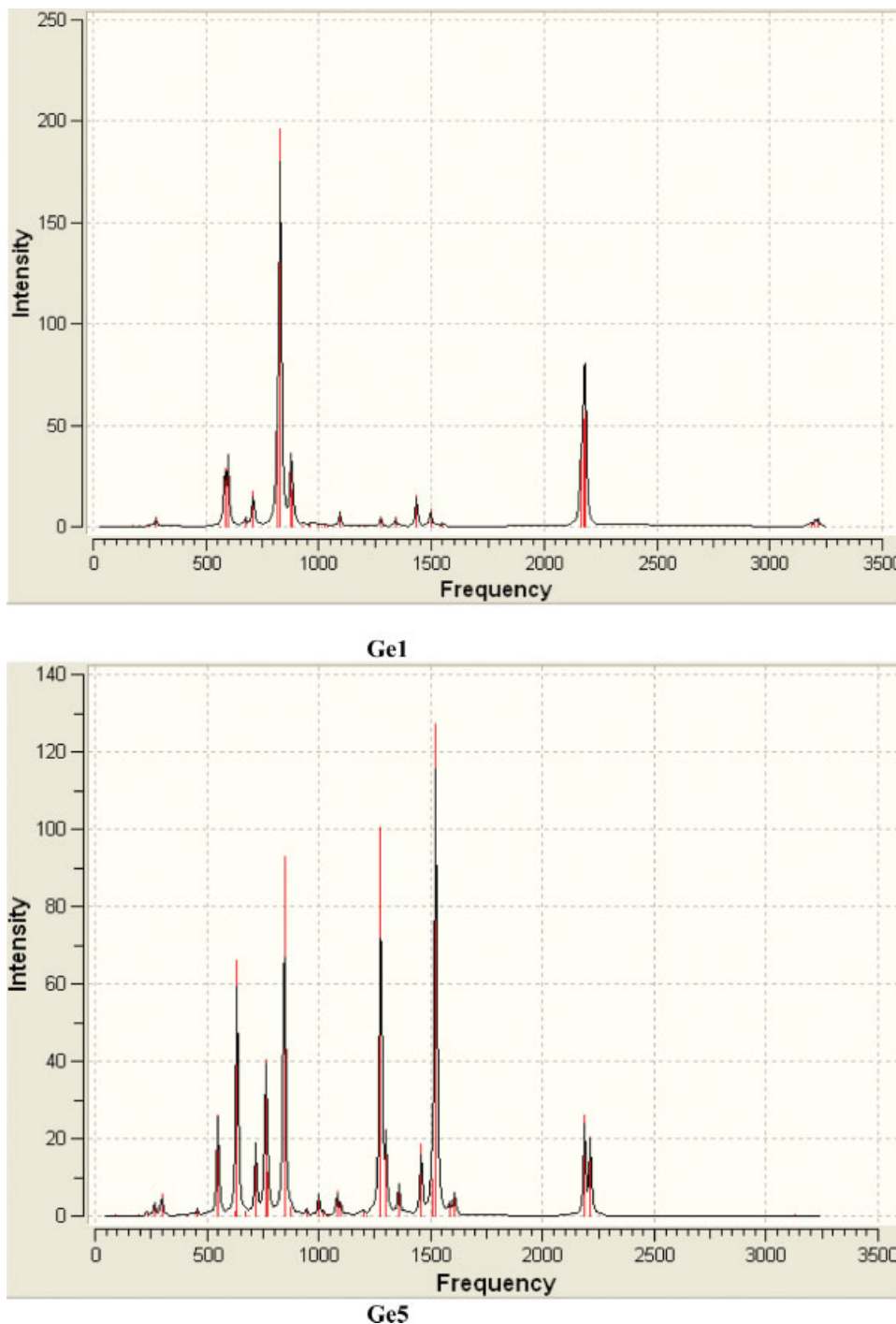
**Figure 3.** Molecular graphs of toluene, its Ni<sup>+</sup> conventional  $\pi$ -complex **C1**, phenylgermane, and the agostic-type **Ge5** complex. Red and yellow dots are bond critical points and ring critical points, respectively. Charge densities at the bcps are in a.u.

of the  $\sigma_{\text{Ge-H}}^*$  antibonding orbitals lead to a significant decrease in the charge density at the bcp of the Ge—H bond involved in the agostic interaction, while new bcps appear between the metal and the corresponding H atom and between the metal and the *ipso* and *ortho* carbon atoms (See Figure 3). The weakening of the Ge—H bond leads to a bond length increase of 0.125 Å (Figure 1) and to a red-shifting of 600 cm<sup>-1</sup> of its stretching frequency. As a consequence, similarly to what was found for the corresponding Cu<sup>+</sup>-complexes one should expect conventional  $\pi$ -complexes and those involving agostic interactions to exhibit quite different infrared spectra, as it is indeed the case (Figure 4). The calculated spectrum for the **Ge5** complex exhibits two strong absorptions at *ca.* 1276 and 1523 cm<sup>-1</sup>, which are not present in the spectrum of the conventional  $\pi$ -complex **Ge1**. These bands correspond, respectively, to the bending and stretching of the X—H bond interacting with the metal which appear strongly shifted to lower frequencies. Accordingly, the band that in complex **Ge1** appears at *ca.* 2182 cm<sup>-1</sup>, which arises from the overlap of the three XH<sub>3</sub> stretching vibrations, is split into two (at 2190 and 2218 cm<sup>-1</sup>, respectively) in the spectrum of the **Ge5** complex, because in this region only the two X—H bonds not interacting with the metal absorb, and their stretching frequencies appear as symmetric and antisymmetric combinations. Taking into account the relative stability of both forms and assuming that the relative

barrier between both species is high enough for both isomers to exist, one should expect the gas-phase spectrum of phenylgermane-Ni<sup>+</sup> complexes to be a superposition of the two aforementioned spectra.

### Binding energies

A comparison of the Ni<sup>+</sup>-binding energies summarized in Table 1 with those of the corresponding Cu<sup>+</sup> complexes, taken from Ref.17, shows that the former are about 1.15 times larger. This clearly reflects the influence of d-orbital occupation on the binding of first-row transition metal ions.<sup>33</sup> In particular, if the d orbital directly pointing to the basic site is occupied, the metal-ligand repulsion leads to lower binding energies. This explains the lower binding energies of Cr<sup>+</sup>, with a d<sup>5</sup> configuration, with respect to those of Sc<sup>+</sup> or V<sup>+</sup>. Following these arguments, one should expect the binding energies to increase from Fe<sup>+</sup> to Ni<sup>+</sup> reflecting a decrease of the ion size. For Cu<sup>+</sup>, however, the binding energy decreases since the d orbital directly interacting with the basic site becomes doubly occupied. The larger second order interaction energies between the occupied and the empty orbitals of both subunits is a second factor, also associated to the small Ni-ligand repulsion, that contributes to enhance the Ni<sup>+</sup> binding energies with respect to Cu<sup>+</sup>, since these energies depend not



**Figure 4.** Calculated infrared spectra (B3LYP/6-311 + G(2df,2p)) for: phenylgermane-Ni<sup>+</sup> conventional  $\pi$ -complex, **Ge1**, and phenylgermane-Ni<sup>+</sup> non-conventional complex **Ge5**. Frequencies are in cm<sup>-1</sup> and intensities in km/mol

only on the energy difference between the interacting orbitals but also on their overlap.

## CONCLUSIONS

The interactions of Ni<sup>+</sup> with toluene, phenylsilane and phenylgermane have significant dissimilarities with those involving Cu<sup>+</sup>. For Ni<sup>+</sup>, the conventional  $\pi$ -complexes

are significantly favored, playing an important role in the PES of the three aromatic derivatives. However, while for toluene only the conventional  $\pi$ -complex should be found in the gas phase, for phenylsilane and phenylgermane, the conventional  $\pi$ -complex and the agostic structure, in which the metal interacts simultaneously with one of the X—H (X = Si, Ge) bonds of the substituent and with the  $\pi$ -aromatic system, present a similar stability. Both type of complexes present quite different infrared spectra

and therefore they could be easily identified using this spectroscopic technique.

The three systems investigated have rather similar Ni<sup>+</sup>-binding energies, which are predicted to be about 1.15 times larger than Cu<sup>+</sup> binding energies, reflecting the effect of the complete occupancy of the *d* orbitals in the latter.

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