Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Mass Spectrometry 227 (2003) 401–412

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Binding energies of Cu^+ to saturated and α,β-unsaturated alkanes, silanes and germanes

The role of agostic interactions

Inés Corral, Otilia Mó, Manuel Yáñez*

Departamento de Química, C-9, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

Received 25 February 2002; accepted 12 June 2002

Abstract

The gas-phase interaction of $H_3C–CH_2–XH_3$ and $H_2C{=}C(H)XH_3$ ($X = C$, Si, 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, the most stable complexes are stabilized through agostic interactions between the metal cation and the hydrogen atoms of the XH_3 group. Only for the unsaturated derivatives, the interaction with the C=C double bond competes with these agostic interactions, although the π-complexes for Si and Ge derivatives are slightly less stable. Since these interactions increase with the hydride character of the hydrogen atoms involved, ethylsilane and ethylgermane are predicted to bind Cu^+ much more strongly than propane. Conversely, vinylsilane and vinylgermane are predicted to have slightly lower Cu^+ binding energies than propene. These agostic interactions lead to a significant weakening of the X–H linkages involved, reflected in a very large red shifting of the X–H stretching frequency. A topological analysis of the charge density of these complexes seems to be a powerful tool to detect and characterize these agostic bonds. Actually, we have found a good correlation between the charge density at the agostic bond critical point and the stability of the complex.

Keywords: Cu^+ affinities; Reactivity of vinylsilanes and germanes; Agostic interactions

1. Introduction

Very little is known on the reactivity of α,β-unsaturated silanes and germanes in the gas phase among other reasons because the synthesis of the latter was described only very recently [1,2] and because some of them are of low stability. As an obvious consequence their intrinsic acidities were reported in the literature only 1 year ago [3], and their proton affinities were theoretically estimated, through the use of density functional theory calculations, also very recently [4]. This latter study showed [4] that these compounds protonate preferentially on the α-carbon atom. More importantly, as a consequence of the intense charge reorganization undergone by the neutral, this proton attachment is followed by a heterolytic bond cleavage. Hence, the product of the protonation

---

* Corresponding author. Tel.: +34-91-397-4953; fax: +34-91-397-4187.

E-mail address: manuel.yanez@uam.es (M. Yáñez).

1387-3806/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1387-3806(03)00083-6

process is a complex between ethylene (or acetylene) and a XH_3^+ (X = Si, Ge) cation.

Due to the non-negligible covalent character of the neutral-Cu^+ interactions [5–9], very often, the Cu^+ complexes resemble closely the corresponding protonated species, where a true covalent bond is formed between the basic center and the incoming proton. This is reflected, for example, in the fact that the nature of the basic center of guanidine [5], formamide [6] or urea [9] does not change when the reference acid is H^+ or Cu^+. However, the α,β-unsaturated silanes and germanes represent a new situation. This can be easily understood if we consider, for example, the $H_2C{=}C(H)XH_3$ (X = Si, Ge) vinyl derivatives. As we have mentioned above, protonation takes place preferentially at C_α yielding $H_2C{=}CH_2 \cdots XH_3^+$ complexes. However, even assuming that attachment of Cu^+ to C_α would be the most favorable process, the product formed, $H_2C{=}CHCu \cdots XH_3^+$ would be very different, and therefore it would not be necessarily the global minimum of the potential energy surface. On the other hand, these compounds present many C–H and X–H linkages which can be involved in typical agostic interactions [10] (vide infra) with the metal cation which are not possible when the attacking ion is a proton.

These possible peculiarities prompted us to investigate the binding of Cu^+ to the aforementioned set of compounds. In order to investigate the effects of the absence of the C=C double bond on the reactivity of the system we have also included in our study the corresponding saturated compounds. We have considered also of interest to compare the behavior of the Si and Ge containing compounds with the corresponding hydrocarbons, in order to analyze the Cu^+ affinity down the group 14 of the periodic table.

2. Computational details

The B3LYP density functional theory approach, as implemented in the Gaussian-98 series of programs [11], which combines Becke's three-parameter non-local hybrid exchange potential [12] with the non-local correlation functional of Lee et al. [13] has been proved to be very well suited for the description of Cu^+ complexes and to obtain Cu^+ binding energies in fairly good agreement with the experimental values [14,15]. In contrast, the most commonly used ab initio approaches are less reliable due to frequent instabilities of the HF wavefunction and to poor convergency of the MPn series [14,16,17]. On the other hand, in general, geometries obtained using the aforementioned DFT method are in fairly good agreement with experimental values [18–25], and, the harmonic vibrational frequencies are closer to experiment than those obtained by using other correlated methods such as MP2 [26,27]. The geometries and harmonic vibrational frequencies of Si and Ge containing compounds were obtained using a 6-311G(d,p) basis set expansion for Cu, while for the remaining atoms a 6-31G(d) basis set was used. The final energies were obtained in single-point calculations carried out at the B3LYP/6-311+G(2df,2p) level.

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 zero point energy (ZPE) corrections, which were scaled by the empirical factor 0.98 [28]. Since one of our main goals is to determine Cu^+ binding energies for $H_2C{=}CHXH_3$ (X = C, Si, Ge) compounds, we have used ethylene as a suitable model system to estimate the accuracy of our theoretical approach. The complexes between ethylene and Cu^+ have been investigated using many different theoretical methods [15,29,30], which yielded D_0 binding energies ranging from 34.6 to 46.5 kcal mol^{-1}. Although the spread of the different experimental estimates was also quite large [30–32], the most recent experimental measurements by Sievers et al. [33] yield a value, 42.0 ± 3 kcal mol^{-1}, which is within the range covered by the different theoretical calculations. Our B3LYP/6-311+G(2df,2p) estimated value is 43.4 kcal mol^{-1} in fairly good agreement not only with the most recent experimental value but also with the most accurate CCSD(T) (42.2 kcal mol^{-1}) ab initio calculations [15].

The atoms in molecules (AIM) theory of Bader [34], was used to investigate the possible bond activations undergone by the neutral upon Cu^+ association and to characterize the possible agostic linkages arising from these interactions. For this purpose we have evaluated the charge density, $\rho(r)$, at the corresponding bond critical points (bcps). 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. The net atomic charges were determined by means of the NBO population analysis [35]. This theoretical procedure was also used to carry out a second order perturbation analysis of the orbital interactions between both interacting systems, in order to characterize the bonding in terms of 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.

3. Results and discussion

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 C_{2v} structures [29]. However, in our case where the presence of a XH_3 (X = C, Si, Ge) substituent breaks the symmetry of the system, we have considered not only the attachment to the π-system, but also the interactions with the CH_2, CH_3 and XH_3 groups. Obviously, for the particular case of the saturated derivatives only these latter interactions are possible.

3.1. Structures, relative stabilities and bonding

The structures of the different $CH_3CH_2XH_3$ saturated and $H_2C{=}CHXH_3$ (X = C, Si, Ge) unsaturated species as well as those of their Cu^+ complexes are given in Fig. 1. Their total energies are summarized in Table 1. Table 1 also contains the calculated binding energies, D_0.

Table 1
Total energies (E, hartrees), zero point energies (ZPE, hartrees) and Cu^+ binding energies (D_0, kcal mol^{-1}) of $CH_3CH_2XH_3$ and $H_2C{=}CHXH_3$ (X = C, Si, Ge) compounds and their Cu^+ complexes

	E[a]	ZPE[b]	D_0 (kcal mol^{-1})[c]
Ethylene	−78.62107	0.0508	–
Ethylene–Cu^+	−1718.87021	0.0539	43.4 (42.0 ± 3)[d]
Propane	−119.18847	0.1030	–
S-C1	−1759.41085	0.1034	28.3
S-C2	−1759.40942	0.1030	27.5
S-C3	−1759.40839	0.1031	27.0
Ethylsilane	−370.58260	0.0898	–
S-Si1	−2010.82105	0.0913	37.7
S-Si2	−2010.80513	0.0894	28.8
S-Si3	−2010.79990	0.0897	25.4
S-Si4	−2010.82519	0.0904	40.8
Ethylgermane	−2158.06536	0.0881	–
S-Ge1	−3798.30694	0.0893	39.8
S-Ge2	−3798.29019	0.0874	30.5
S-Ge3	−3798.28344	0.0879	26.0
S-Ge4	−3798.31060	0.0881	42.9
Propene	−117.95359	0.0793	–
U-C1	−1758.20915	0.0818	47.8
U-C2	−1758.16793	0.0792	23.6
U-C3	−1758.14291	0.0802	7.3
Vinylsilane	−369.34657	0.0667	–
U-Si1	−2009.59765	0.0689	45.2
U-Si2	−2009.58739	0.0674	39.7
U-Si3	−2009.56420	0.0680	24.8
U-Si4	−2009.59865	0.0686	46.0
Vinylgermane	−2156.82817	0.0649	–
U-Ge1	−3797.08166	0.0670	46.8
U-Ge2	−3797.07028	0.0648	41.0
U-Ge3	−3797.05543	0.0662	30.8
U-Ge4	−3797.08245	0.0665	47.6

[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).
[d] Experimental value taken form ref. [33].

3.2. Saturated compounds

The first conspicuous fact from Fig. 1 is that, for the saturated compounds, the interaction of Cu^+ with the CH_2, CH_3 and XH_3 groups leads to stable structures which are local minima of the corresponding potential energy surface (PES). For propane, the global

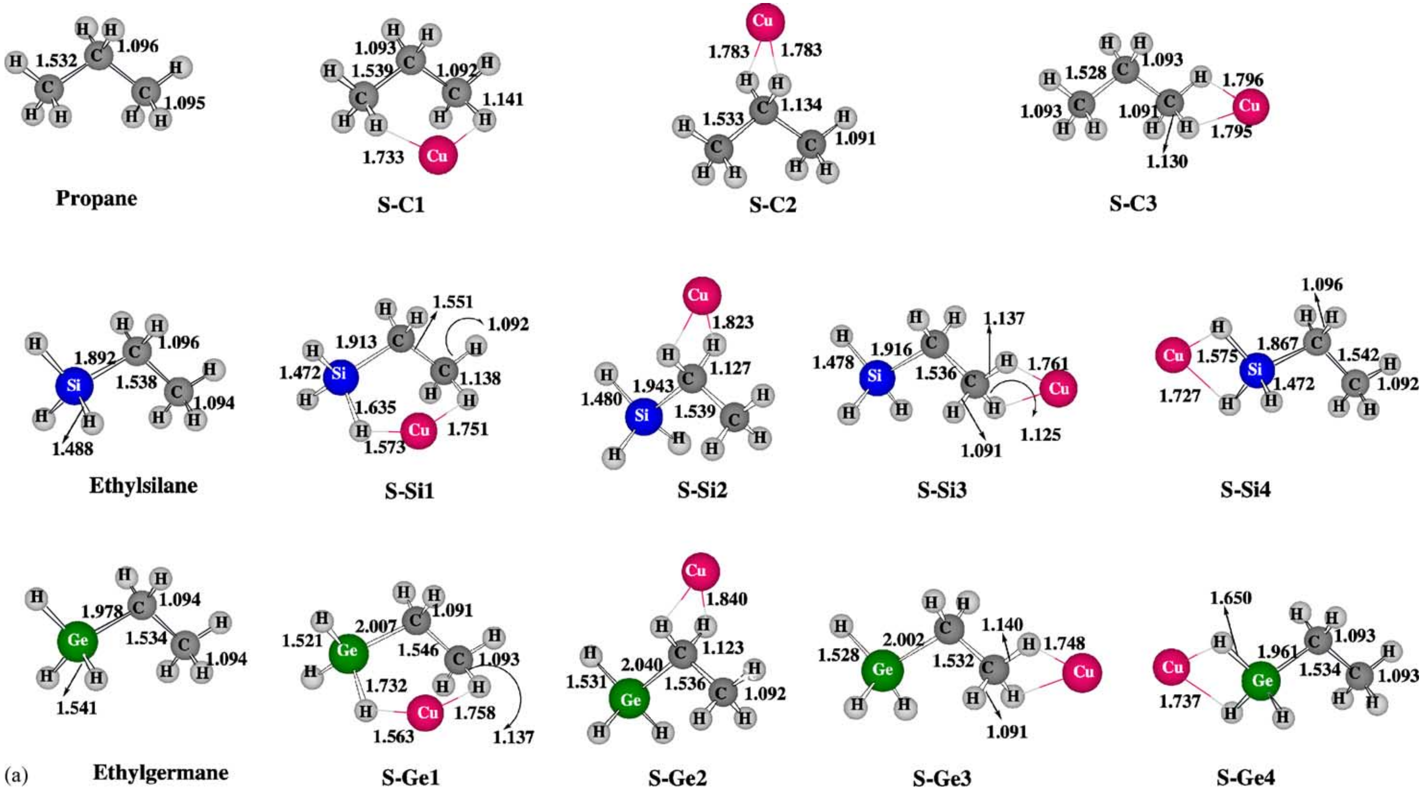


Fig. 1. B3LYP/6-311G(d,p) optimized geometries of $CH_3CH_2XH_3$ and $H_2C{=}CHXH_3$ (X = C, Si, Ge) and their Cu^+ complexes. Bond lengths in Å and bond angles in degrees (°).

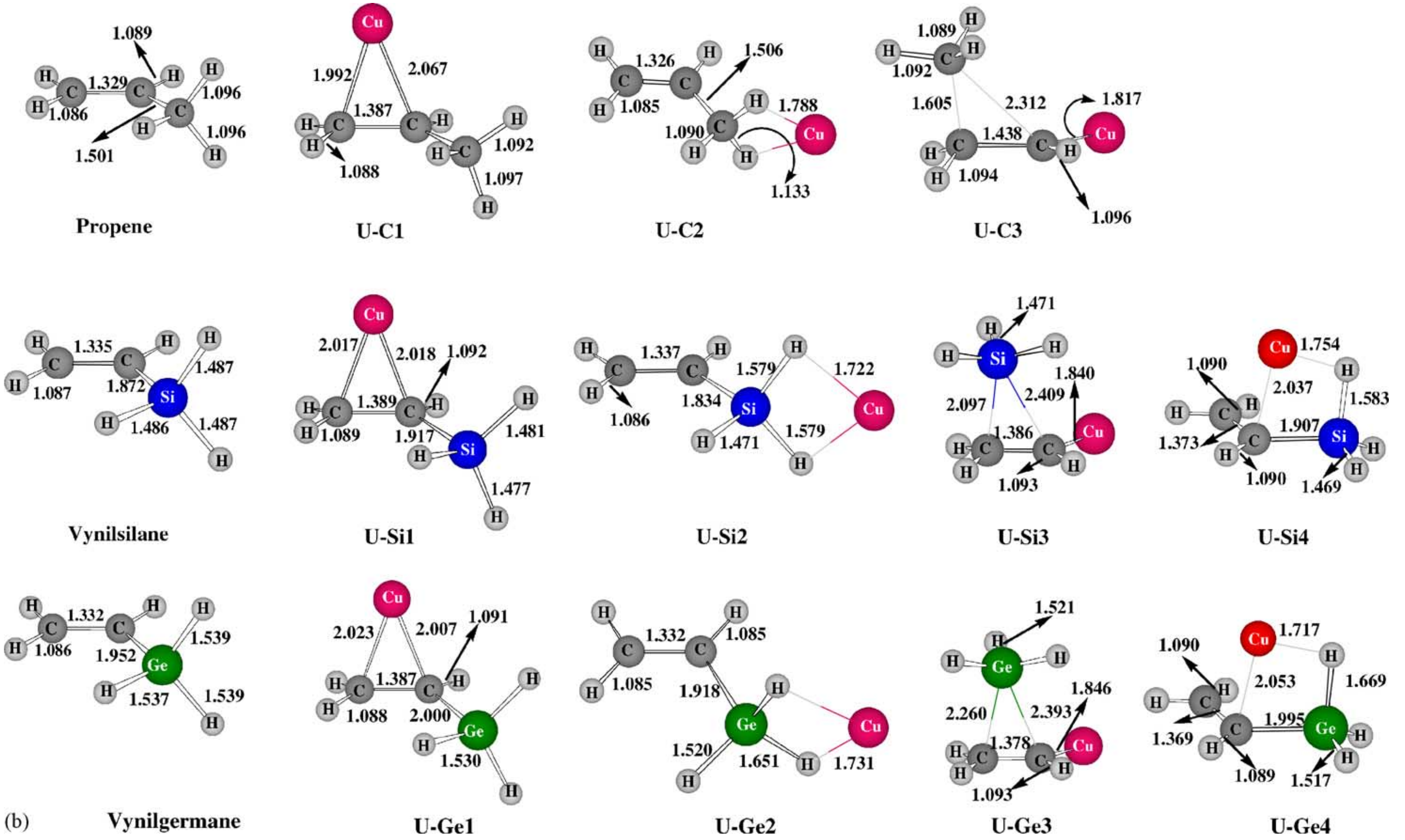
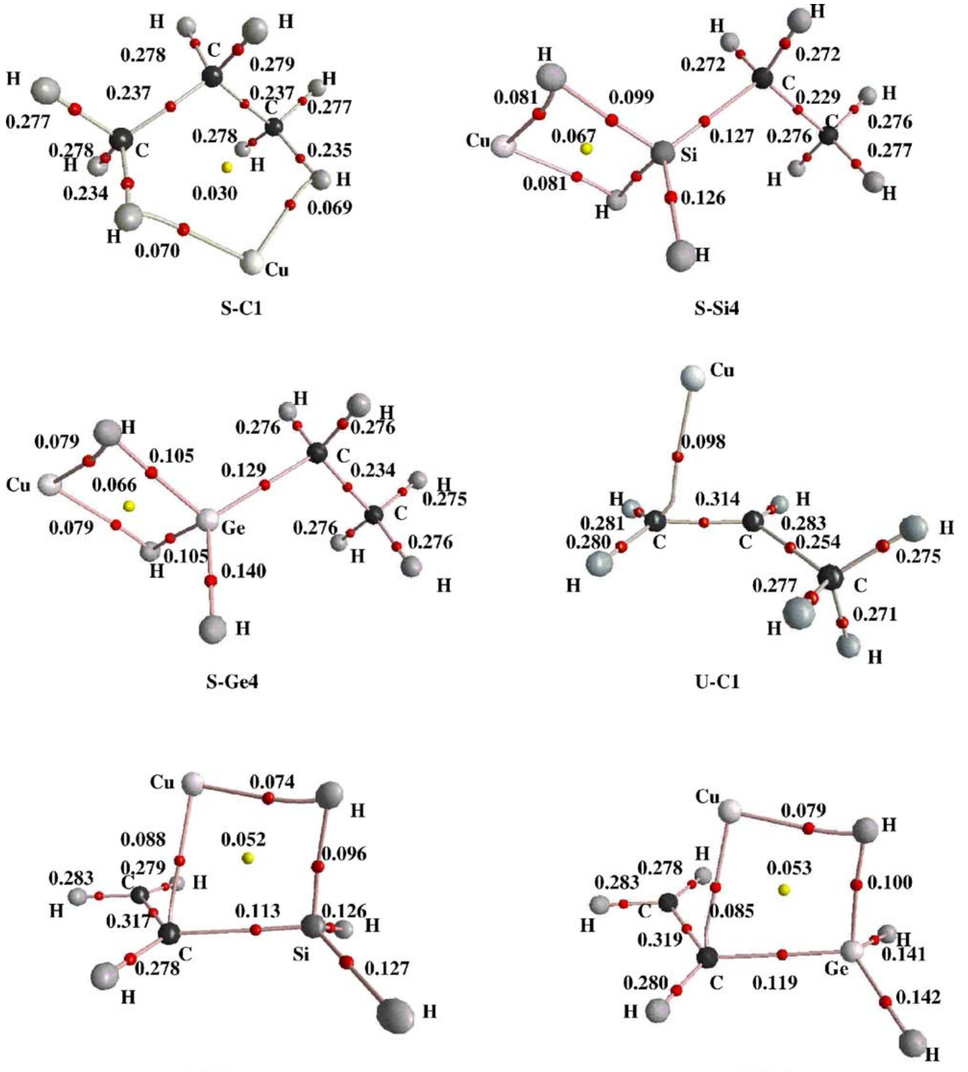


Fig. 1. (*Continued*).

minimum, **S-C1**, corresponds to a complex in which the Cu^+ interacts simultaneously with the two terminal CH_3 groups. It should be emphasized that although structure **S-C1** was already described in the literature [36], the other two local minima, not considered in previous calculations, namely **S-C2** and **S-C3**, are predicted to be only 0.7 and 1.3 kcal mol^{-1} less stable, respectively. Similar results were reported previously in the literature for $Co(C_3H_8)^+$ complexes [37]. However, for Cu^+–C_2H_6 the analogous to **S-C3** complex was found not to be a stationary point of the potential energy surface [38]. As we shall discuss latter, the stability of these latter structures can be explained in terms of the nature of the interaction. Conversely, although for ethylsilane and ethylgermane, the structures in which Cu^+ interacts with the CH_3 and the XH_3 simultaneously, namely **S-Si1** and **S-Ge1**, are also local minima of the PES, complexes **S-Si4** and **S-Ge4** in which Cu^+ interacts exclusively with the XH_3 group (X = Si, Ge), are predicted to be about 3 kcal mol^{-1} more stable, and accordingly the global minima of the PES. In all cases, the less stable complex, **S-C3**, **S-Si3** and **S-Ge3** corresponds to that in which Cu^+ is attached to one CH_3 group exclusively.

As far as the most stable complexes are concerned another significant difference between propane and its Si- and Ge-containing analogs is that the latter exhibit Cu^+ binding energies more than 10 kcal mol^{-1} higher than the former. To understand these differences it is necessary to gain some insight into the nature of the bonding in each case. It has been claimed in the literature [29] that the interaction between Cu^+ and alkanes is essentially electrostatic. However, as we have already mentioned in Section 1, different theoretical studies showed [6,8,9] that these interactions have a non-negligible covalent character when the compound has basic centers other than carbon atoms. A topological analysis of the charge density of the complexes under scrutiny shows the existence of bond critical points between Cu^+ and two of the hydrogen atoms of the groups with which it interacts (see Fig. 2). These kinds of interactions where named as agostic by Brookhart and Green [10], after unusual low field shifts in the ^{1}H-NMR spectrum [39] as well as C–H bond lengthening [40], reduced C–H stretching frequencies [40], and remarkably short metal–hydrogen distances [41] were observed in many transition metal complexes. These non-conventional bonds were described by Cotton et al. [41] as three-center-two-electron bonds, similar to the ones responsible for the bonding in diborane or for the bonding in many protonated alkanes [42–45] or in the protonated form of P_4 [46], 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, together with a back-donation from a filled metal d orbital to the X–Y σ^* antibonding orbital was proposed [47]. This orbital picture is similar to that reported previously [37] to explain the bonding between Co^+ and H_2, where the $1\sigma_g$ orbital of H_2 acts as a donor to the empty 4s orbital of the Co^+, whereas there is a back-bonding involving charge transfer from an occupied Co^+ d_{yz} orbital to the H_2 antibonding orbital ($1\sigma_u$). This alternative picture led Nikonov et al. [48] to consider more appropriate the term three-center-n-electrons ($2 \leq n < 4$) to describe these bonds. The existence of the two aforementioned $H \cdots Cu$ bcps in the complexes investigated is consistent with both models, and the existence of a ring critical point (see Fig. 2) for structures **S-C1**, **S-Si1** and **S-Ge1** corroborates that they are cyclic complexes. On the other hand the analysis of intermolecular attractive orbital interactions carried out by means of a NBO analysis confirms the three-center-n-electrons ($2 \leq n < 4$) model. Let us take complex **S-C1** as a suitable example, a second order NBO orbital interaction analysis shows the existence of a donation from the C–$H_{a,b}$ σ bonding orbitals (the subscripts a and b identify the two hydrogens involved in the agostic interaction) to a vacant orbital of Cu associated with an interaction energy of 14 kcal mol^{-1}. Concomitantly, there is a backdonation from a filled orbital of Cu toward the C–$H_{a,b}$ σ^* antibonding orbitals, with an interaction energy of 4.7 kcal mol^{-1}.

On the other hand, it has been pointed out [49] that agostic interactions must involve an electron rich X–H group and an electron-deficient species, in our case Cu^+. This would immediately explain the enhanced



S-C1 **S-Si4**

S-Ge4 **U-C1**

U-Si4 **U-Ge4**

Fig. 2. Molecular graphs of the most stable Cu^+ complexes of $CH_3CH_2XH_3$ and $H_2C{=}CHXH_3$ (X = C, Si, Ge) derivatives showing the bond paths, the position of the bond critical points, ring critical points and the charge density (e a.u.$^{-3}$) evaluated at these points at the B3LYP/6-311G(d,p) level.

Cu^+ binding energies of the Si- and Ge-derivatives with respect to propane, because the agostic hydrogens of the former have a net negative charge (see Table 2), while the hydrogen atoms of propane are positively charged. These differences are clearly reflected in the charge densities at the agostic H · · · Cu bcp, which for Si–H · · · Cu or Ge–H · · · Cu interactions are much greater than for C–H · · · Cu ones (see Fig. 2). For the same reason the interaction with two hydrogens of the XH_3 group, in complexes **S-Si4** and **S-Ge4**, should be expected to be favored with respect to the simultaneous interaction with the CH_3 and the XH_3 group, in complexes **S-Si1** and **S-Ge1**. Our results also indicate that **S-C2**, **S-Si2**, **S-Ge2** complexes in which Cu^+ in-

Table 2
NBO net charges of the hydrogen atoms of the CH_2 and XH_3 groups of $CH_3CH_2XH_3$, $H_2C=CHXH_3$ (X = C, Si, Ge) compounds and their most stable Cu^+ complexes

Group	$CH_3CH_2XH_3$					
	X = C	**S-C1**	X = Si	**S-Si4**	X = Ge	**S-Ge4**
XH_3	+0.19	+0.10	−0.17	−0.23[a]	−0.13	−0.21[a]
CH_2	+0.18	+0.23	+0.22	+0.25	+0.21	+0.24
	$H_2C=CHXH_3$					
	X = C	**U-C1**	X = Si	**U-Si4**	X = Ge	**U-Ge4**
XH_3	+0.20	+0.24	−0.16	−0.27[a]	−0.12	−0.25[a]

[a] Net charge of the H atom involved in the agostic interaction.

teracts with the $–CH_2$ group are slightly more stable than complexes **S-C3**, **S-Si3**, **S-Ge3**, in which Cu^+ interacts with the terminal methyl group.

The enhanced agostic interaction in the case of Si- and Ge-derivatives with respect to the propane is also reflected in a more efficient donation from the XH bonding orbital to the metal and a more efficient back donation from the metal to XH antibonding orbital. In fact, the second order NBO orbital interaction analysis indicates that while for **S-C1** the energies associated with such interactions, as indicated above, are 14 and 4.7 kcal mol^{-1}, respectively, for **S-Si1** the analogous orbital interaction energies involving the Si–H bonding and antibonding molecular orbitals are: 45.1 and 11.5 kcal mol^{-1}, respectively. For **S-Ge1** the corresponding values are 53.9 and 13.7 kcal mol^{-1}, respectively. These differences are nicely reflected in the lengthening of the X–H bonds. Since the back-donation from Cu toward the Si–H (or Ge–H) σ^* antibonding orbital of the SiH_3 (or GeH_3) group of ethylsilane (or ethylgermane) is more efficient than toward the C–H σ^* antibonding orbital of propane, the lengthening of the Si–H (or Ge–H) bond is also higher than that undergone by the C–H bond of propane. Indeed, considering the most stable complex in each case one observes that while the C–H bond in propane lengthens by 0.046 Å upon Cu^+ attachment, the Si–H and the Ge–H bond lengths of ethylsilane and ethylgermane increase by 0.087 and 0.109 Å, respectively. Concomitantly, the charge densities at the corresponding C–H, Si–H and Ge–H bcps decrease significantly on going from the neutral (C = 0.272, Si = 0.118, Ge = 0.133 e a.u.$^{-3}$) to the Cu^+-complex (C = 0.234, Si = 0.099, Ge = 0.105 e a.u.$^{-3}$), while the net negative charge at the hydrogen atom increases, in absolute value, also significantly (see Table 2). Also consistently, the stretching frequencies of the CH (or XH) bonds involved in the agostic interaction are significantly shifted to lower frequencies. For **S-C1**, this shifting is close to 470 cm^{-1} (see Table 3), and the two C–H stretching modes directly perturbed by Cu^+ association appear as in-phase and out-of-phase combinations, completely independent of the remaining C–H stretching modes which are practically unaffected. For ethylsilane and ethylgermane the shiftings of the Si–H and the Ge–H stretching frequencies upon formation of complexes **S-Si4** and **S-Ge4**, are higher (447 and 498 cm^{-1}, respectively). This weakening of two of the X–H bonds is accompanied by a slight reinforcement of the C–X linkage, whose stretching frequency appears blue shifted (see Table 3).

Finally, it is important to emphasize that in all cases, consistently with the three-center bonding model discussed above, Cu^+ interacts systematically with two hydrogen atoms, even though $Cu^+–CH_4$ complexes were predicted to have C_{3v} symmetry [50]. However, this result should be taken with care because more accurate calculations [37] indicated, for instance, that $Co^+–CH_4$ complexes have C_{2v} symmetry. This applies also to complex **S-C1**, in which Cu^+ interacts only with one hydrogen of each of the terminal methyl groups. A similar complex involving Co^+ was described in the literature [37] as coordination of the metal cation to four C–H bonds. Very likely, in view of our results for Cu^+, the coordination to two C–H bonds would be found more stable if the symmetry constrains imposed in the geometry optimization were removed.

It is also worth noting that there is a rough relationship between the charge density at the H···Cu bcp and the relative stability of the complex. As indicated before, the lowest charge density corresponds to agostic linkages between Cu^+ and CH bonds, in

Table 3
Harmonic vibrational frequencies (cm^{-1}) of $CH_3CH_2XH_3$, $H_2C{=}CHXH_3$ (X = C, Si, Ge) compounds and their most stable Cu^+ complexes

Assignment	$CH_3CH_2XH_3$					
	X = C	**S-C1**	X = Si	**S-Si4**	X = Ge	**S-Ge4**
CH_3 stretching	3084	3126	3087	3114	3091	3120
	3081	3074	3080	3112	3075	3107
	3018	2559[a]	3022	3043	3019	3040
CH_2 stretching	3034	3094	3052	3078	3034	3100
	3014	3057	3019	3036	3067	3058
XH_3 stretching	3083	3123	2217	2302	2129	2188
	3071	3071	2213	1781[a]	2125	1643[a]
	3015	2534[b]	2212	1753[b]	2122	1611[b]
C–C stretching	871[c]	852[c]	982	972	980	970
C–X stretching	1057[d]	1042[d]	597	652	514	553
	$H_2C{=}CHXH_3$					
	X = C	**U-C1**	X = Si	**U-Si4**	X = Ge	**U-Ge4**
XH_3 stretching	3092	3131[e]	2226	2331	2134	2228
	3056	3115[e]	2214	2294	2127	2196
	3013	3086	2218	1707[f]	2128	1514[g]
CH_2 stretching (asymmetric)	3208	3203	3187	3203	3186	3198
CH_2 stretching (symmetric) + CH stretching	3127	3108	3115	3099	3126	3097
	3120		3105	3117	3106	3131
C=C stretching	1712	1570	1656	1561	1656	1560
C–X stretching	924	902	618	587	527	501

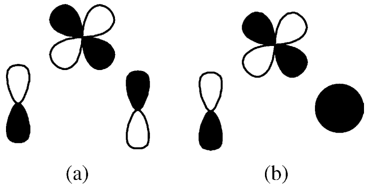
[a] In-phase combination of the stretching modes of the two C–H bonds involved in the agostic interaction.
[b] Out-of-phase combination of the stretching modes of the two C–H bonds involved in the agostic interaction.
[c] CCC symmetric stretch.
[d] CCC asymmetric stretch.
[e] These CH_3 stretching modes are strongly coupled with the stretch of the CH group.
[f] Stretching of the Si–H bond involved in the agostic interaction.
[g] Stretching of the Ge–H bond involved in the agostic interaction.

agreement with the fact that propane exhibits the lowest Cu^+ binding energy (see Table 1). However, in spite of the fact that ethylgermane has a value of D_0 2 kcal mol^{-1} higher than ethylsilane, the charge density at the Ge···H agostic bonds in complex **S-Ge4** is slightly smaller than that found for Si···H interactions in complex **S-Si4**.

Finally, it should be mentioned that similar agostic interactions involving Si–H bonds have been reported [48,51] in half-sandwich complexes of Nb and Ta, as well as in other complexes containing different transition metals.

3.3. *Unsaturated compounds*

The differences between propene and its Si- and Ge-containing analogs are also dramatic. As illustrated in Fig. 1 and Table 1, the most stable $H_2C{=}CHCH_3$–Cu^+ complex, **U-C1**, corresponds to a structure in which the metal cation interacts directly with the π-system, while for vinylsilane and vinylgermane such a structure (**U-Si1** and **U-Ge1**) corresponds to the second stable minimum, the global minimum (**U-Si4** and **U-Ge4**) being a complex in which the metal interacts simultaneously with the π-system and



Scheme 1.

with one of the hydrogen atoms of the XH_3 group. It is also important to note that complexes similar to **U-Si4** and **U-Ge4** are not stationary points of the PES in the case of propene as they collapse to the global minimum **U-C1**.

The bonding in complexes **U-C1**, **U-Si4** and **U-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 two p orbitals of the C=C carbons (see Scheme 1a). In the second case this interaction involves a p orbital of C_α and the s orbital of the hydrogen atom of the XH_3 group (see Scheme 1b).

Consistently, a topological analysis of their charge densities shows the existence of bond critical points between Cu and C_α and between Cu and a H atom of the XH_3 group, as well as a ring critical point (see Fig. 2). The formation of these three-center-*n*-electron bonds should significantly perturb the C=C bond. Actually, in all cases the charge density at the C=C bcp decreases (C $=$ 0.030, Si $=$ 0.021, Ge $=$ 0.021 e a.u.$^{-3}$), the bond length increases (C $=$ 0.058, Si $=$ 0.038, Ge $=$ 0.037 Å) and the stretching frequency appears red-shifted (C $=$ 142, Si $=$ 95, Ge $=$ 96 cm^{-1}). As expected these effects are higher for propene where both carbons of the C=C bond participate in the interaction. For vinylsilane and vinylgermane, there is also a strong perturbation of the corresponding Si–H and Ge–H bonds, respectively. As shown in Fig. 1, the bond length increases (Si $=$ 0.096, Ge $=$ 0.130 Å), the charge density at the bcp decreases (Si $=$ 0.023, Ge $=$ 0.033 e a.u.$^{-3}$), and the X–H stretching frequencies appear red shifted by 511 and 614 cm^{-1}, respectively (see Table 3). In contrast with what was found for the saturated analogs, the C–X stretching frequency appears slightly shifted to the red.

It can be also observed that the binding of Cu^+ to the XH_3 group of the unsaturated compounds to yield complexes **U-C2**, **U-Si2** and **U-Ge2** is slightly less exothermic than for the corresponding saturated analogs, reflecting the higher electronegativity of the H_2C=CH-group as compared with the H_3C–CH_2–one.

It is also interesting to note that the Cu^+ binding energy for propene is predicted to be 4.5 kcal mol^{-1} higher than that of ethylene, clearly reflecting the inductive effect of the methyl substituent, as well as the increase in the polarizability of the system. In this respect it is worth to remember that in general gas-phase proton affinities increase by about 6 kcal mol^{-1} upon methyl substitution [52,53]. It is also obvious from the values in Table 1, that this effect is slightly smaller when the substituent is a –SiH_3 or a –GeH_3 group, reflecting a poorer inductive effect for groups containing second or third row atoms. The main consequence of this is that while propane was predicted to be significantly less basic than ethylsilane and ethylgermane with regards to Cu^+, propene is predicted to be slightly more basic than vinylsilane or vinylgermane.

3.4. Cu^+ association vs. proton attachment

Finally, it would be interesting to compare the Cu^+ attachment processes with the corresponding proton attachments. As we have already mentioned, quite often the structure of Cu^+ complexes resembles closely the structure of the corresponding protonated species, and also quite often the most basic site in protonation processes is also the site which binds more strongly Cu^+. However, propene, vinylsilane and vinylgermane are clear exceptions. In a recent paper [4], 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 ethylene and the corresponding XH_3^+ (X $=$ C, Si, Ge) cation. Similarly to what was found for the protonation process, attachment of Cu^+ to C_α also leads to the cleavage of the C_α–XH_3

bond leading to complexes **U-C3**, **U-Si3** and **U-Ge3**. It must be observed, however, that while in the protonated species the XH_3^+ cation sits above the middle point of the $H_2C{=}CH_2$ moiety for symmetry reasons, in the case of the Cu^+ complexes the XH_3^+ is closer to the β carbon due to its repulsion with the metal. Also, while for protonation this is the most exothermic process, due to the great stability of the molecule of ethylene formed, in this case this corresponds to the less exothermic reaction, as a consequence of the relative lower stability of the $H_2C{=}CHCu$ moiety formed.

4. Conclusions

In the interactions between $H_3C–CH_2–XH_3$ and $H_2C{=}C(H)XH_3$ (X = C, Si, 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. Actually, these interactions are responsible for the structure and stability of the Cu^+ complexes involving saturated compounds. Since these interactions increase with the hydride character of the hydrogen atoms involved, ethylsilane and ethylgermane are predicted to bind Cu^+ much more strongly than propane. For propene, however, the interaction with the π-system clearly dominates and the corresponding π-complex, **U-C1** is much more stable than **U-C2** in which Cu^+ exhibits an agostic interaction with the methyl group. Conversely, for vinylsilane and vinylgermane, the corresponding π-complexes, **U-Si1** and **U-Ge1** are slightly less stable than complexes **U-Si4** and **U-Ge4**, where Cu^+ interacts simultaneously with C_α and with a hydrogen atom of the XH_3 group.

These agostic interactions can be viewed as the result of a donation from a X–H (X = C, Si, Ge) σ bonding orbital of the neutral moiety toward an empty orbital of Cu^+ and a backdonation from filled orbitals of Cu^+ toward a X–H σ* antibonding orbital of the neutral. As a consequence, they lead to a very large weakening of the X–H linkages involved. These effects, which are stronger for Si- and Ge-containing groups than for C-containing groups, are mirrored in a significant increase of the X–H bond length, a decrease of the charge density at the bcp and a very large red shifting of the X–H stretching frequency. A topological analysis of the charge density of these complexes seems to be a powerful tool to detect and characterize these agostic bonds.

For the unsaturated compounds, and similarly to what was found in the corresponding protonation processes, attachment of the metal cation to C_α is followed by a C–X bond cleavage, so that the ion formed can be viewed as tightly bound complex between a $H_2C{=}CHCu$ moiety and the corresponding XH_3^+ cation. However, in contrast with protonation where the corresponding $H_2C{=}CH_2 \cdots XH_3^+$ complexes were the global minima of the potential energy surface, the $H_2C{=}CHCu \cdots XH_3^+$ complexes exhibit a rather low stability.

Acknowledgements

This work has been partially supported by the DGI Project No. BQU2000-0245. A generous allocation of computational time at the CCC of the Universidad Autónoma de Madrid is also acknowledged. I. C. gratefully acknowledges a FPU grant from the Ministerio de Educación, Cultura y Deporte of Spain.

References

[1] J.-C. Guillemin, L. Lassalle, T. Janati, Planet. Space Sci. 43 (1995) 75.
[2] A. Chrostowska, V. Métail, G. Pfister-Guillouzo, J.-C. Guillemin, J. Organomet. Chem. 570 (1998) 175.
[3] J.-F. Gal, M. Decouzon, P.-C. Maria, A.I. González, O. Mó, M. Yáñez, S. El Chaouch, J.-C. Guillemin, J. Am. Chem. Soc. 123 (2001) 6353.
[4] O. Mó, M. Yáñez, J.-F. Gal, P.-C. Maria, J.-C. Guilleminm, J. Phys. Org. Chem. 15 (2002) 509.
[5] A. Luna, B. Amekraz, J.P. Morizur, J. Tortajada, O. Mó, M. Yáñez, J. Phys. Chem. A 101 (1997) 5931.
[6] A. Luna, B. Amekraz, J. Tortajada, J.P. Morizur, M. Alcamí, O. Mó, M. Yáñez, J. Am. Chem. Soc. 120 (1998) 5411.
[7] M. Alcamí, O. Mó, M. Yáñez, A. Luna, J.P. Morizur, J. Tortajada, J. Phys. Chem. A 102 (1998) 10120.
[8] A. Luna, M. Alcamí, O. Mó, M. Yáñez, Int. J. Mass Spectrom. 201 (2000) 215.

[9] A. Luna, B. Amekraz, J.P. Morizur, J. Tortajada, O. Mó, M. Yáñez, J. Phys. Chem. A 104 (2000) 3132.

[10] M. Brookhart, M.L.H. Green, J. Organomet. Chem. 250 (1983) 395.

[11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. González, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. González, M. Head-Gordon, E.S. Replogle, J.A. Pople, 1999.

[12] A.D. Becke, Phys. Rev. A 38 (1988) 3098.

[13] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.

[14] A. Luna, M. Alcamí, O. Mó, M. Yáñez, Chem. Phys. Lett. 320 (2000) 129.

[15] S.J. Klippenstein, C.-N. Yang, Int. J. Mass Spectrom. 201 (2000) 253.

[16] M. Alcamí, O. Mó, M. Yáñez, Mass Spectrom. Rev. 20 (2001) 195.

[17] T.K. Ghanty, E.R. Davidson, Int. J. Quant. Chem. 77 (2000) 291.

[18] F. Sim, A. St-Amant, I. Papai, D.R. Salahub, J. Am. Chem. Soc. 114 (1992) 4391.

[19] K. Kim, K.D. Jordan, J. Phys. Chem. 98 (1994) 10089.

[20] C.W. Bauschlicher Jr., Chem. Phys. Lett. 246 (1995) 40.

[21] A.L. Llamas-Saiz, C. Foces-Foces, O. Mó, M. Yáñez, E. Elguero, J. Elguero, J. Comput. Chem. 16 (1995) 263.

[22] C.W. Bauschlicher Jr., H. Partridge, J. Chem. Phys. 103 (1995) 1788.

[23] A.M. Mebel, K. Morokuma, M.C. Lin, J. Chem. Phys. 103 (1995) 7414.

[24] J.A. Montgomery Jr., M.J. Frisch, J.W. Ochterski, G.A. Peterson, J. Chem. Phys. 110 (1999) 2822.

[25] L.A. Curtiss, P.C. Redfern, K. Raghavachari, J.A. Pople, J. Chem. Phys. 114 (2001) 108.

[26] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.

[27] M.W. Wong, Chem. Phys. Lett. 256 (1996) 391.

[28] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502.

[29] M. Sodupe, C.W. Bauschlicher Jr., S.R. Langhoff, H. Partridge, J. Phys. Chem. 96 (1992) 2118.

[30] R.H. Hertwig, W. Koch, D. Schröder, H. Schwarz, J. Hrusak, P. Schwerdtfeger, J. Phys. Chem. 100 (1996) 12253.

[31] R.C. Burnier, G.D. Byrd, B.S. Freiser, Anal. Chem. 52 (1980) 1641.

[32] E.R. Fisher, P.B. Armentrout, J. Phys. Chem. 94 (1990) 1680.

[33] M.R. Sievers, L.M. Jarvis, P.B. Armentrout, J. Am. Chem. Soc. 120 (1998) 1891.

[34] R.F.W. Bader, Atoms in Molecules: A Quantum Theory, Clarendon Press, Oxford, 1990.

[35] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.

[36] Y.D. Hill, B.S. Freiser, C.W. Bauschlicher Jr., J. Am. Chem. Soc. 113 (1991) 1507.

[37] J.K. Perry, G. Ohanessian, W.A. Goddard III, J. Phys. Chem. 97 (1993) 5238.

[38] M. Rosi, C.W. Bauschlicher Jr., S.R. Langhoff, H. Partridge, J. Phys. Chem. 94 (1990) 8656.

[39] S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 6288.

[40] S. Trofimenko, J. Am. Chem. Soc. 90 (1968) 4754.

[41] F.A. Cotton, T. LaCour, A.G. Stanislowski, J. Am. Chem. Soc. 96 (1974) 754.

[42] J.W.M. Carneiro, P.V.R. Schleyer, M. Saunders, R. Remington, H.F. Schaefer III, A. Rauk, T.S. Sorensen, J. Am. Chem. Soc. 116 (1994) 3483.

[43] A.L.L. East, Z.F. Liu, C. McCague, K. Cheng, J.S. Tse, J. Phys. Chem. A 102 (1998) 10903.

[44] M.N. Glukhovtsev, R.D. Bach, Chem. Phys. Lett. 286 (1998) 51.

[45] S.J. Collins, P.J. O'Malley, J. Chem. Soc., Faraday Trans. 92 (1996) 4347.

[46] J.L.M. Abboud, M. Herreros, R. Notario, M. Esseffar, O. Mó, M. Yáñez, J. Am. Chem. Soc. 118 (1996) 1126.

[47] M.D. Butts, J.C. Bryan, X.-L. Luo, G. Kubas, Inorg. Chem. 36 (1997) 3341.

[48] G.I. Nikonov, P. Mountford, S.K. Ignatov, J.C. Green, M.A. Leech, G.L. Kuzmina, A.G. Razuvaev, N.H. Rees, A.J. Blake, J.A.K. Howard, D.A. Lemenovskii, J. Chem. Soc., Dalton Trans. (2001) 2903.

[49] P.L.A. Popelier, G. Logothetis, J. Organomet. Chem. 555 (1998) 101.

[50] G. Berthier, R. Cirimaglia, A. Daoudi, H. Mestdagh, C. Rolando, M. Suard, J. Mol. Struct. (Theochem.) 254 (1992) 43.

[51] G.I. Nikonov, J. Organomet. Chem. 625 (2001) 24.

[52] J. Catalan, J.L.G. De Paz, M. Yáñez, R.M. Claramunt, C. Lopez, J. Elguero, F. Anvia, J.H. Quian, M. Taagepera, R.W. Taft, J. Am. Chem. Soc. 112 (1990) 1303.

[53] NIST Chemsitry Webbook Standard, Release No. 69, July 2001.