DFT Description of Binary Metal Met-Cars $Ti_xZr_yC_{12}$ ($x + y = 8$) and of Some Conformers of the M_6C_{12}, M_7C_{12}, and M_8C_{13} Clusters (M = Ti, Zr)

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Density functional calculations including nonlocal corrections to the exchange and correlation energies have been carried out on mono- and bimetallic metallocarbohedrenes (met-cars) of titanium and zirconium $Ti_xZr_yC_{12}$ ($y = 0, 1, 3, 4, 5, 8$; $x + y = 8$), as well as on the endohedral and exohedral conformations of Ti_8C_{13} and on Ti_7C_{12}. For all considered molecules, geometry optimizations have been carried out assuming for the metal framework the structure of tetracapped tetrahedron with two distinct sets of metal sites which has been consistently computed to be the most stable one for Ti_8C_{12} and related species. For mixed-metal met-cars, zirconium atoms have been assigned to occupy either sites of the capped tetrahedron or sites of the capping tetrahedron, thus generating two conformers for each value of y different from 0 or 8. The total energies of those pairs of conformers have been found to differ by less than 1.5 kcal mol^{-1} for all considered bimetallic stoichiometries. This similar behavior of the two sets of metallic sites regarding the single or multiple substitution of Ti by Zr could explain the regular distribution of the peaks in the mass spectra of $Ti_xZr_yC_{12}$ ($y = 0-5$), which had been interpreted up to now as providing evidence that the eight metal atoms were actually equivalent. At variance from metal substitution, metal dissociation is found very sensitive to the site to which the removed atom belongs. The present study confirms that the structure of tetracapped tetrahedron assumed for Ti_8C_{12} is extremely favorable to the encapsulation of an extra carbon atom. Exohedral conformations are less stable due to the presence of two unpaired electrons on the extra carbon. The computed electron affinity (1.26 eV) and ionization potential (4.6 eV) of Ti_8C_{12} are in agreement with values or estimates recently reported from experiment. It finally appears that none of the properties of Ti_8C_{12} and other met-cars reported to date are in contradiction with the assumption of a tetrahedral structure with two distinct sets of metal sites.

1. Introduction

A series of studies carried out by Castleman's group have revealed the existence of a new class of transition-metal carbide clusters known as metallocarbohedrenes, or met-cars.[1−5] Met-car clusters are characterized by a 2:3 metal-to-carbon ratio, and the most prominent species, characterized by a "supermagic" peak at the mass spectrometer, has been identified as M_8C_{12} with M = Ti, V, Zr, Hf,[1−5] Nb,[6] Cr, Mo, and Fe.[7] The specific stability of those 20-atom clusters has been immediately interpreted in terms of a fullerene-like cage structure with T_h symmetry composed of 12 C−M−C−C−M pentagons (pentagonal dodecahedron, Figure 1a).[1] Some time later, several independent investigations carried out by means of DFT,[8−10] Hartree−Fock,[11,12] and configuration interaction[13,14] levels of theory suggested that the pentagonal dodecahedron was not the most stable conformation of M_8C_{12} and could even represent a local maximum on the potential energy hypersurface.[15] Several other cage structures, all characterized by a ±45° rotation of the six C_2 ligands with respect to the underlying face of a distorted M_8 cube, were computed to be local minima.[11,13] The most stable among those 36 M−C bond structures, first described by Dance,[8] is characterized by a tetrahedral distortion of the metal framework yielding a cluster with T_d symmetry (Figure 1b). The eight metal atoms, all equivalent in the pentagonal dodecahedron, are split in the tetrahedral form into two sets of equivalent metal sites, each occurring four times. A

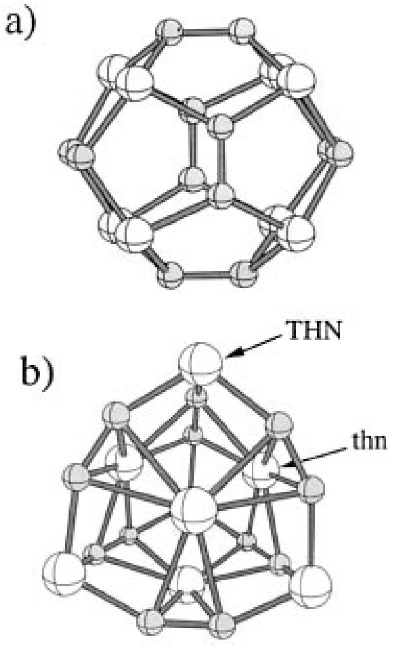

Figure 1. (a) Structure of pentagonal dodecahedron (T_h symmetry) initially proposed for met-cars. (b) Structure of tetracapped tetrahedron (T_d symmetry) predicted to be the most stable one from various theoretical calculations.

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TABLE 1: Total Bond Energies, Bond Energies per Atom (eV), Stabilization Energies with Respect to Ti_8C_{12} ($-\Delta E$, eV), and Stabilization Energies per Substituted Metal Atom ($-\Delta E/y$, eV) for Ti_8C_{12} and for Some Zr-Substituted Met-Cars $Ti_xZr_yC_{12}$ ($y = 1, 3, 4, 5, 8$; $x + y = 8$)[a]

met-car	position of Zr atoms	symmetry	total bond energy	bond energy per atom	$-\Delta E$	$-\Delta E/y$
Ti_8C_{12}		T_d	−131.227	6.561	0.0	0.0
Ti_7ZrC_{12}	*thn*	C_{3v}	−131.943	6.597	0.716	0.716
Ti_7ZrC_{12}	**THN**	C_{3v}	−131.904	6.595	0.677	0.677
$Ti_5Zr_3C_{12}$	*thn*	C_{3v}	−133.338	6.667	2.111	0.704
$Ti_5Zr_3C_{12}$	**THN**	C_{3v}	−133.383	6.669	2.156	0.719
$Ti_4Zr_4C_{12}$	*thn*	C_{3v}	−133.999	6.700	2.772	0.693
$Ti_4Zr_4C_{12}$	**THN**	C_{3v}	−133.977	6.699	2.750	0.687
$Ti_3Zr_5C_{12}$	*thn* (4) **THN** (1)	C_{3v}	−134.546	6.727	3.319	0.664
$Ti_3Zr_5C_{12}$	**THN** (4) *thn* (1)	C_{3v}	−134.501	6.725	3.274	0.655
Zr_8C_{12}		T_d	−136.294	6.815	5.067	0.633

[a] Two conformers, characterized by the atomic sites of metal substitution *thn* (capped tetrahedron) or **THN** (capping tetrahedron), have been considered for all mixed-metal species.

controversy focused on the shape of the M_8C_{12} cage being either T_h or T_d has developed since then, and the interpretation of the met-car properties in terms of either a fully symmetric framework or two distinct sets of metal sites represents a key point for obtaining evidence in favor of one or the other structures.[16−27] A strong argument was provided in favor of the pentagonal dodecahedron isomer by the production of a series of binary metal met-cars with general formula $Ti_xZr_yC_{12}$ ($x + y = 8$, $y = 1-5$).[26,27] The purely statistical variation of the peak intensities associated with y varying from 0 to 5 was interpreted as providing evidence that the eight metal sites are actually equivalent. It was argued that models displaying nonequivalent sets of metal sites would predict unfavorable stoichiometries of $Ti_5Zr_3C_{12}$ and $Ti_3Zr_5C_{12}$, resulting in an abrupt truncation in the mass distribution at that point. This interpretation obviously implies that the bonding energy of one or several Zr atoms in a mixed-metal met-car with 36 M−C bonds is different when Zr occupies either the sites of the capped tetrahedron of metal atoms (*thn)* or those of the capping ones (**THN**). If the bonding energies of metal atoms for the two sets of sites of the T_d structure were close enough, the distribution of the peak intensities of binary metal clusters in the mass spectrum would certainly behave as if the coordination of all metal atoms were equivalent. Since that point has never been investigated yet, we report DFT calculations, geometry optimizations, and computed bond energies for the following clusters: Ti_8C_{12}, Ti_7ZrC_{12}, $Ti_6Zr_2C_{12}$, $Ti_5Zr_3C_{12}$,$Ti_4Zr_4C_{12}$, and Zr_8C_{12}. The dissociation of one and two metal atoms from Ti_8C_{12} and Zr_8C_{12}, the subsequent relaxation of the M_7C_{12} and M_6C_{12} clusters, and the ionization energies of M_8C_{12} have also been investigated, to help in interpreting the delayed ionization and the delayed atomic ion emission recently observed for Ti_8C_{12}[28] and other met-cars.[29] Finally, we report the computed electron affinities of M_8C_{12} (M = Ti, Zr), to be compared with the lowest energy peak observed in the photoelectron spectrum of $(Ti_8C_{12})^-$,[25] and the structures and energies of the exohedral and endohedral conformers of the Ti_8C_{13} cluster.

2. Computational Details

All calculations have been carried out by means of density functional calculations including gradient corrections. We used the local spin density approximation characterized by the electron gas exchange (Xα with $\alpha = {}^2/_3$) together with Vosko−Wilk−Nusair[30] parametrization for correlation. Becke's nonlocal corrections to the exchange energy[31] and Perdew's nonlocal corrections to the correlation energy[32] have been added. The choice of this model is justified by its efficiency and accuracy in the evaluation of bond energies for a variety of metal−ligand and metal−metal bonds, as documented by Rosa and colleagues.[33] Those calculations have been carried out with the ADF program,[34] using triple-ζ + polarization Slater basis sets to describe the valence electrons of C, N, O, and H. For metal atoms, a frozen core composed of the 1s to 2sp shells for titanium and 1s to 3spd shells for zirconium was described by means of single Slater functions. The *n*s and *n*p electrons were described by double-ζ Slater functions, the *n*d and ($n + 1$)s by triple-ζ functions, and ($n + 1$)p by a single orbital.[35,36] As in the very accurate work of Rosa et al.[33] on the dissociation of $Mn_2(CO)_{10}$, it was not found necessary to supplement the metal basis set with f-type polarization functions. Spin-unrestricted calculations were used for the open-shell configurations. Quasi-relativistic corrections were employed using the Pauli formalism with corrected core potentials. The quasi-relativistic frozen core shells were generated using the auxilliary program DIRAC. [34]

3. Results and Discussion

3.1. Mixed-Metal Met-Cars $Ti_xZr_yC_{12}$. The bond energies obtained for the $Ti_xZr_yC_{12}$ clusters ($y = 0, 1, 3, 5, 8$; $x + y = 8$), assuming for the metal framework a structure of tetracapped tetrahedron with C_{3v} symmetry, are reported in Table 1. Two conformations have been considered for each stoichiometry and their geometries optimized. Those conformations differ by attributing the Zr atoms either the sites of the *capped* tetrahedron of metal atoms, referred to as *thn*, or the sites of the *capping* tetrahedron, referred to as **THN.** The bond energies per atom, the stabilization energies $-\Delta E$ with respect to Ti_8C_{12}, and the stabilization energies per substituted atom $-\Delta E/y$ are displayed in Table 1.

Contrary to the conjecture proposed by Cartier and colleagues,[26,27] no special stability is observed for $Ti_4Zr_4C_{12}$ with respect to $Ti_5Zr_3C_{12}$ and to $Ti_3Zr_5C_{12}$. ΔE is negative and steadily decreasing when y increases, which means that the replacement of titanium by zirconium results in a stabilization of the complex. The stabilization energy per substituted atom $-\Delta E/y$ steadily declines when y increases from 0.68/0.72 eV for $y = 1$ to 0.63 eV for $y = 8$ (Table 1). For all considered values of y, the total energy of the complex depends very little on the site, *thn* or **THN**, selected for substitution. Even though the two conformations optimized for each considered value of y correspond to distinct isomers, as shown in Figure 2 for $y = 4$, the energies associated with those isomers never differ by more than 1.2 kcal mol^{-1}. For $y = 4$, this difference is computed to be 0.6 kcal mol^{-1}, which means that the two considered isomers, and possibly others, are expected to coexist. Those results led to the conclusion that the relative peak heights of the mass spectra of the $Ti_xZr_yC_{12}{}^+$ species[26,27] should not be

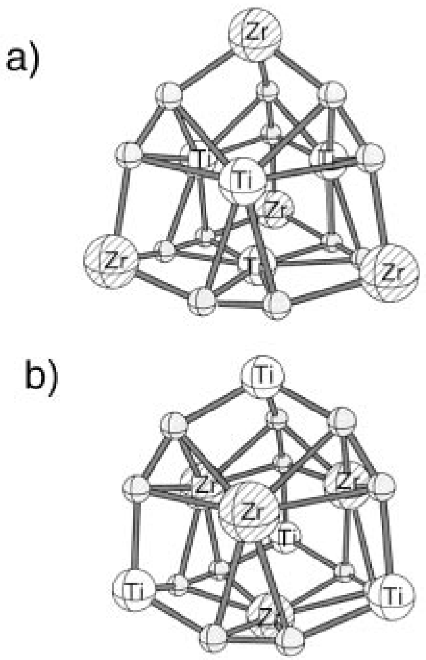

Figure 2. The two conformers considered for $Ti_4Zr_4C_{12}$: (a) the four titanium atoms are on the capped tetrahedron *thn*; (b) the four Ti atoms are on the capping tetrahedron **THN.**

TABLE 2: Computed Properties of M_8C_{12} (M = Ti, Zr): Electron Affinity (EA), Ionization Potential (IP), and Dissociation Energies (ΔE) Associated with the Processes $M_8C_{12} \rightarrow (M_7C_{12})^{thn} + M$ and $M_8C_{12} \rightarrow (M_7C_{12})^{THN} + M$[a]

	EA	IP	$\Delta E(M_7C_{12})^{thn}$	$\Delta E(M_7C_{12})^{THN}$
Ti_8C_{12}	1.26	4.60	8.262 (8.214)[b]	10.12
Zr_8C_{12}	1.05	4.10	9.03	10.33

[a] The superscripts *thn* for the capped tetrahedron of metal atoms and **THN** for the capping one characterize the missing site. All values in eV. [b] Value obtained by considering the Jahn−Teller distortion from C_{3v} to C_s.

significantly influenced by the existence of two distinct sets of metal atoms.

3.2. Electron Affinity, Ionization Energy of Single-Metal Met-Cars, and Metal Dissociation Processes. The recent observation of delayed ionization (thermoionic emission) and delayed atomic ion emission channels for Ti and V metallocarbohedrenes[28] as well as for the binary metal met-cars $Ti_xM_yC_{12}$ (M = Zr, Nb; $0 \leq y \leq 4$; $x + y = 8$)[29] has raised interest for an accurate determination of the ionization energy and of the metal dissociation energy in those species. Computed values for those quantities as well as for electron affinities are reported in Table 2 for the single-metal met-cars M_8C_{12} (M = Ti, Zr) assuming the tetrahedral conformation with lowest energy.

The electron affinity computed for Ti_8C_{12} after reoptimization of $(Ti_8C_{12})^-$ is 1.26 eV (Table 2). This value compares well to the electron affinity of 1.05 ± 0.05 eV deduced from the first peak of the photoelectron spectrum of $(Ti_8C_{12})^-$ recently reported by Wang et al.[25] However, neither the DFT calculations recently carried out by Dance[15] agree with the orbital diagram of Lin and Hall[12] taken by Wang as a basis for the interpretation of the photoelectron spectra, nor do those of the present work.

The HOMO of the DFT calculations is a triply degenerate orbital, partly occupied with two electrons for neutral Ti_8C_{12} and with three electrons for $(Ti_8C_{12})^-$, thus yielding a quartet ground state for the anion. Those results are not in contradiction with previous Hartree−Fock (HF) and CI calculations carried out in our group,[13,14] but they present some differences we should explain. In the HF approach the electronic configuration of Ti_8C_{12} corresponding to the 80 valence electrons is

$$(3a_1)^2(4e)^4(3t_1)^6(6t_2)^6(4a_1)^1(7t_2)^3$$

with four open-shell d-metal electrons accommodated in d_{z^2}-like metal orbitals of symmetry a_1 and t_2, which belongs to the small tetrahedron *thn*. Therefore, at one configuration HF level the ground state is a quintet with four electrons localized on the four apexes of the inner tetrahedron. CI calculations considering the correlation of the 20 metal valence electrons showed that these four electrons are spin-coupled, resulting in quasi-degenerate $^1A_1$ and $^3T_1$ states with high occupancy for orbital $4a_1$.[13,14] The main difference between the present DFT calculations and the ab initio results concerns the localized/delocalized nature of the d-metal electrons. The treatment of Ti and C valence electrons at the same accuracy level including electron correlation leads to a more covalent description of the titanium−carbon interactions. In the DFT approach, there is not the presence of four unpaired electrons clearly localized on a set of titanium atoms as was found at the HF level. Another feature of the DFT results is that there are several configurations in a small range of energy, since HOMO $4t_1$ and LUMO $7t_2$ are quasi-degenerate orbitals. Then, even though the more stable configuration is the triplet

$$(3a_1)^2(4e)^4(3t_1)^6(6t_2)^6(4a_1)^2(4t_1)^2(7t_2)^0$$

with two unpaired electrons on the orbital $4t_1$, the alternative configurations $...(4a_1)^2(4t_1)^1(7t_2)^1$ and $...(4a_1)^2(4t_1)^0(7t_2)^2$ are higher than the ground state by only 0.07 and 0.17 eV, respectively. Certainly, the excited triplet with two electrons on $7t_2$ resembles very much the $^3T_1$ state obtained at the HF/CI level.

The computed *vertical* ionization potential of Ti_8C_{12} is 4.7 eV. Geometry relaxation of the cation leads to an *adiabatic* IP for Ti_8C_{12} of 4.6 eV (Table 2). This value is similar to the one obtained by Dance assuming the same conformation[37] but lower than the ionization potentials previously computed by Reddy et al. for the dodecahedral structure (6.02 eV).[38] The computed IP of 4.7 eV is in very good agreement with preliminary measurements by Duncan which indicate a low value of 4.9 ± 0.2 eV.[39a] Calculations on Zr_8C_{12} and its associated monocation predict that the IP of the Zr met-car is lower than the ionization potential of the Ti analogue, the computed *vertical* and *adiabatic* ionization potentials being 4.2 and 4.1 eV, respectively. No significant differences were observed when the IP is computed assuming a D_{2d} structure for Zr_8C_{12}. Dance has also found a low IP for the Zr met-car (3.99 eV).[40] The theoretical values seem to be in disagreement with the studies of Brock and Duncan, who find that Zr_8C_{12} ionizes when the laser photon energy is higher than 5.76 eV. The discrepancies between the experimental and theoretical IP's only concern the Zr cluster, since preliminary calculations of the *vertical* ionization potentials of V_8C_{12} (5.5 eV) and Nb_8C_{12} (5.4 eV) are consistent with the prediction that the vanadium and niobium met-cars have higher IP's than that of the titanium met-car.[39a] It must be also remarked that the IP determinations of Brock and Duncan are indirect and that their results do not discard a low IP of Zr_8C_{12}.[39b]

Finally, it seems that no reliable estimate of the energy change associated with the dissociation of one metal atom from Ti_8C_{12} has been given yet. The value of 6.62 eV proposed by Reddy et al.[38] and referred to in the discussion concerning the mechanism of the atomic ion emission of Ti_8C_{12}[28,29] corresponds

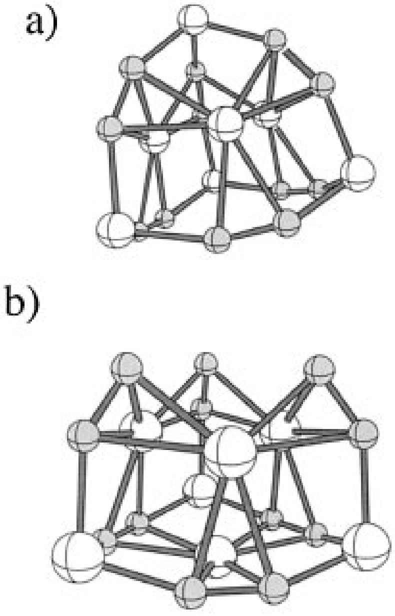

Figure 3. The two conformers of Ti_7C_{12}: (a) the metal atom has been removed from *thn*; (b) the metal atom has been removed from **THN**.

to an average stabilization energy per atom and cannot be assimilated to the difference between the energy of Ti_8C_{12} in its ground state and optimized geometry and the energy of Ti_7C_{12} in a similar situation. Two isomers of Ti_7C_{12} first assumed to have C_{3v} symmetry can be obtained by deleting one metal atom from either *thn* or **THN**.

Expelling one atom from the capped tetrahedron yields the most stable isomer, referred to as $(Ti_7C_{12})^{thn}$ (Figure 3a), and this process is endothermic by 8.26 eV (Table 2). The ground state of $(Ti_7C_{12})^{thn}$ assuming a C_{3v} symmetry is computed to be a triplet with a doubly degenerate HOMO accommodating two electrons. A Jahn−Teller distortion can therefore be predicted toward a singlet ground state with C_s symmetry. Lowering the symmetry constraints to C_s indeed yields a singlet state corresponding to a slightly distorted geometry and more stable than the above-mentioned triplet state by 1.1 kcal mol^{-1} (Table 2).

Removing a Ti atom from the *capping* tetrahedron leaves three acetylenic dicarbon ligands with one dangling bond each (Figure 3b). Quite reasonably, the corresponding isomer, $(Ti_7C_{12})^{\mathbf{THN}}$, is higher in energy, by 1.86 eV, than the conformer of Figure 3a, and the associated dissociation process would be endothermic by 10.12 eV (Table 2). Those values, and the following ones, refer to the triplet state obtained under the C_{3v} symmetry constraints; the Jahn−Teller distortion has not been considered. Therefore, the computed energy for the first dissociation step is 8.21 eV. This value is in complete agreement with the upper limit of 9 eV given by Kerns et al.[41]

Since the successive dissociation of two single metal atoms has been proved possible for $Ti_8C_{12}^{+}$ [42] and for binary metal met-cars $Ti_7MC_{12}^{+}$ (M = Zr, Nb, Y),[43] it is of interest to consider the process of removing a second metal atom:

$$(Ti_7C_{12})^{thn} \rightarrow Ti_6C_{12} + M$$

The calculations have been carried out assuming Ti_6C_{12} to have C_{3v} symmetry and the second metal to be expelled from a **THN** site, thus again generating three dangling bonds. The energy required for this second dissociation step is 10.67 eV. The dissociation of a second carbon originating, as the first one, in the capped tetrahedron and yielding a Ti_6C_{12} isomer with C_s symmetry now appears more probable.

Expelling one metal atom from Zr_8C_{12} requires more energy than the equivalent process in Ti_8C_{12}: 9.03 eV instead of 8.26 eV (C_{3v} symmetry). This result, together with the bond energies per atom reported in Table 1 for Ti_8C_{12} and Zr_8C_{12}, suggests that Zr is more strongly attached to the cluster than Ti in single-metal met-cars. This could help in explaining the result of photofragmentation experiments on the binary metal cluster $Ti_7ZrC_{12}^{+}$, evidencing channels for the successive loss of two titanium atoms but no distinct channel attributable to Zr loss.[43]

The values reported in the present work for the ionization potentials and for the dissociation energies of M_8C_{12} (M = Ti, Zr) in their conformation with T_d symmetry comply with the condition

$$\mathrm{IP} \leq E_{\mathrm{diss}}$$

imposed on those quantities in order for the M_8C_{12} clusters to undergo thermionic emission.[28,29]

3.3. Endohedral and Exohedral Addition of a Carbon Atom to M_8C_{12} (M = Ti, Zr). Evidence of the existence of the titanium met-car molecule of 21 atoms, $Ti_8C_{13}^{+}$, was first provided by Wei et al. from mass spectra.[4] The stability of Ti_8C_{13} obtained by formally encapsulating a carbon atom in the Ti_8C_{12} cage of tetrahedral symmetry has also been predicted by Pilgrim and Duncan, from an analysis of the dissociation products of the fcc crystallite $Ti_{14}C_{13}^{+}$.[44] The local density calculations reported by Lou and Nordlander[10] confirmed the propensity of an endohedral carbon to further increase the stability of the met-car cluster. The binding energy predicted by Lou and Nordlander for the central carbon encapsulated in the Ti_8C_{12} cage with T_d symmetry amounts to 7.7 eV. Moreover, a closed-shell conformation is obtained for the ground state of neutral Ti_8C_{13} together with a substantial increase of the ionization potential (6.3 eV) and of the HOMO−LUMO gap with respect to the hollow cage. A more recent DFT calculation by Dance introducing the nonlocal corrections confirms those trends,[37] even though the binding energy of the central carbon is reduced to 5.4 or 5.1 eV depending on the nonlocal density functional. Other structural isomers could be considered however for the Ti_8C_{13} cluster if the extra carbon atom is assumed to be exohedral. The possible existence of an exohedral conformer has been substantiated by ion mobility experiments reported by Lee et al.[17] The modeling of the ion mobility observed for $Ti_8C_{13}^{+}$ from assumed structural parameters provides excellent agreement with the observed data when the extra carbon atom occupies the external coordination site of one Ti atom, whereas the mobility modeled from an endohedral structure significantly deviates from experiment.[17] The endohedral and the exohedral models investigated by Lee et al. both assume for the Ti_8C_{12} framework a dodecahedral structure with equivalent metal atoms. Since no calculation has been reported to date on the exohedral conformers of Ti_8C_{13}, we have optimized the two structures of minimal energy where the exohedral carbon is coordinated to a metal atom belonging either to *thn* (Figure 4a) or to **THN** (Figure 4b). An equivalent optimization has been carried out on the endohedral structure (Figure 4c). Similar calculations have been performed on the three equivalent conformers of Zr_8C_{13}. The results are displayed in Table 3.

The aggregation of an extra carbon to M_8C_{12} yields local energy minima for all considered conformations. However, the endohedral conformation, which leads to a closed-shell electronic configuration, stabilizes the extra carbon by 5.8 eV, whereas the stabilization provided by both possible exohedral conformations is lower than 4 eV. The high stability of the endohedral form suggests that this conformation of $Ti_8C_{13}^{+}$ is

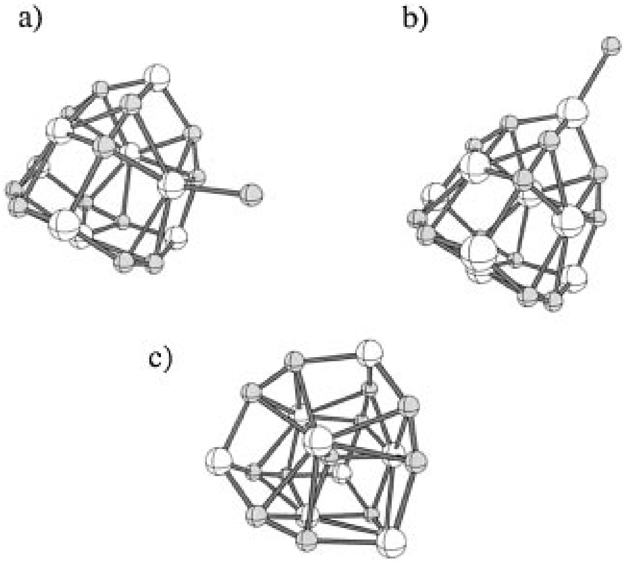

Figure 4. The three conformers of Ti_8C_{13}: (a) exohedral conformation, C attached to an atom of *thn*; (b) exohedral conformation, C attached to an atom of **THN**; (c) endohedral conformation.

TABLE 3: Bond Energy per Atom (eV) and Binding Energy of the Extra Carbon Atom $E_{C_{13}}$ Computed for the Endohedral and for the Two Exohedral Conformers of M_8C_{13} (M = Ti, Zr)

conformer		total bond energy	bond energy per atom	$E_{C_{13}}$
Ti_8C_{12}		−131.227	6.56	
Ti_8C_{13}	endo	−137.002	6.52	5.77
	exo (*thn*)	−134.614	6.41	3.39
	exo (**THN**)	−134.890	6.42	3.66
Zr_8C_{12}		−136.294	6.81	
Zr_8C_{13}	endo	−142.649	6.79	6.35
	exo (*thn*)	−139.915	6.66	3.62
	exo (**THN**)	−140.104	6.67	3.81

the one generated from the dissociation of $Ti_{14}C_{13}^+$. However, our results are not in contradiction with the possibility for an exohedral conformation of $Ti_8C_{13}^+$ to be directly created in the LAVA source. This possibility is supported by reactivity experiments recently carried out on $Ti_8C_{13}^+$ and $Ti_{14}C_{13}^+$ ions generated under those conditions.[20] The ground state of both exohedral conformations is a triplet state, the two unpaired electrons being localized on the extra carbon. Note that no unpaired electron remains localized on the metal framework, at variance from what is predicted by DFT calculations for neutral Ti_8C_{12}. This can be interpreted by means of a two-electron charge transfer from Ti_8C_{12} to the extra carbon and by the subsequent σ-donation interaction between a carbon dianion in its triplet state and the met-car dication $(Ti_8C_{12})^{2+}$, which is closed shell. The unpaired electrons of the carbon dianion can be considered as dangling bonds, a situation in sharp contrast to the perfect electron pairing obtained for the *endo* conformation. Although the Mulliken population analysis evidences in this latter case too an important charge transfer toward the endohedral carbon, the presence in neutral Ti_8C_{12} of four metal electrons distributed on the apexes of the capped metal tetrahedron and the existence of a quintet state coupling those four metal electrons at a relatively low energy[13,14] provide an electronic environment extremely favorable to the encapsulation of a carbon atom.

4. Summary and Conclusion

The possibility offered by calculations including correlation energy to compare the intrinsic stabilities of molecules made with different atoms has been used to investigate the series of mono- and bimetallic met-cars $Ti_xZr_yC_{12}$ ($y = 0, 1, 3, 4, 5, 8$; $x + y = 8$). The structure assumed for all clusters is derived from the conformation of a tetracapped tetrahedron of metal atoms first proposed by Dance for Ti_8C_{12} and giving rise to two sets of metal sites, *thn* and **THN**, each occurring four times.[8] The total binding energies computed for the series of met-cars are steadily increasing with the number *y* of substituted Zr atoms. Contrary to the prediction made by Cartier, May, and Castleman, no special stability is observed for the $Ti_4Zr_4C_{12}$ stoichiometry.[26] The computed stabilities of the mixed-metal systems are practically unaffected by the site of substitution, for all considered values of *y*. Regarding the substitution of Ti by Zr, met-car clusters should therefore behave as if the two possible substitution sites were indiscernible. This probably explains the regularity of the mass peaks recorded for the series Ti_x-Zr_yC_{12} ($y = 0-5$) produced under direct laser vaporization conditions with Ti:Zr molar ratios of the target mixture varying from 2:1 to 12:1.[26,27]

At variance from the metal substitution process, the dissociation energy of one metal atom strongly depends on the metal site. For Ti_8C_{12}, dissociation of one metal atom requires 1.85 eV less when the titanium atom is taken out of the small tetrahedron. The high cost of a metal extraction from the outer tetrahedron is attributed to the breaking of three Ti−C σ-bonds without subsequent removal of the dangling bonds on the carbon atoms. Finally, the $Ti_8C_{13}^+$ cluster that has been characterized as the most intense band in the photodissociation spectrum of the 3 × 3 × 3 crystallite $Ti_{14}C_{13}^+$ [43] should be assigned the endohedral conformation $C@Ti_8C_{12}^+$. The two possible structures corresponding to an exohedral conformation of the extra carbon are both local energy minima, which suggests that those structures could be formed if the central position is not easily accessible. However, the valence shell of the exohedral carbon remains incomplete with two unpaired electrons. This is at variance from the endohedral structure and explains the much larger stability of the latter conformation.

Remembering that the DFT modeling of met-car adducts with T_d symmetry accounts for the recently observed reactivity of those clusters,[45] it now appears that the structure of tetracapped tetrahedron cannot be ruled out anymore on the basis of the observed properties of met-cars.

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