Ab Initio SCF and CI Investigations on Titanium–Carbon Clusters: Metallocarbohedrenes Ti$_8$C$_{12}$ and Fcc Crystallites Ti$_{14}$C$_{13}$

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Abstract: Ab initio Hartree–Fock calculations have been carried out at the SCF and configuration interaction (CI) levels on Ti$_8$C$_{12}$, and at the SCF level on Ti$_{14}$C$_{13}$. For Ti$_8$C$_{12}$, the cage structure of tetracapped tetrahedron of metal atoms with T_d symmetry and 36 Ti–C bonds was found to be most stable at both levels of calculation. A proper localization of the d metal electrons rather than the aufbau principle is defined as a decisive criterion for selecting the ground-state electronic configuration. A one-configuration SCF calculation accounting for this localization criterion leads to a quintet ground state and to an optimal geometry characterized by $d_{C-C} = 1.343$ Å, $d_{Ti-C(end-on)} = 1.964$ Å, $d_{Ti-C(side-on)} = 2.265$ Å, and $d_{Ti-Ti} = 2.943$ and 3.114 Å. CI calculations allowing for a coupling of the four unpaired electrons lead to a totally symmetric singlet ground state, separated from the quintet state by 10.5 kcal mol^{-1}. The electronic structure of the Ti$_8$ framework is discussed in terms of mixed valency, the metal atoms belonging to either tetrahedral sets being assigned the formal oxidation states III or 0, respectively. An interchange process between both tetrahedral sets through an intermediate structure of pentagonal dedocahedron with T_h symmetry is subject to a considerable energy barrier. The energy minimum corresponding to the T_d symmetry is not unique, however. Six other minima, corresponding all to cage structures with 36 Ti–C bonds have been characterized on the potential energy hypersurface. CI calculations show that those secondary minima are less stable than the T_d form by 153 to 179 kcal mol^{-1}. The calculations carried out on the Ti$_{14}$C$_{13}$ cluster indicate that a proper localization of the d metal electrons requires the O_h symmetry of the fcc crystallite to be broken into T_d. This leads to metal–carbon bond lengths comprised between 1.99 Å and 2.12 Å in the optimized structure. Breaking the O_h symmetry leads to a potential energy curve with two equivalent minima separated by an energy barrier of 13 kcal mol^{-1} associated with the totally symmetric O_h structure.

I. Introduction

The recent discovery of highly stable metal–carbon clusters corresponding to the stoichiometry M$_8$C$_{12}$ (M = Ti, V, Zr, Hf,[1] Cr, Mo, Fe[2]) has triggered a number of experimental[3] and theoretical[4–11] investigations concerning this class of "metallic buckyballs".[12] Most studies indeed agree to predict for those new molecules the shape of a nearly spherical cage, even though a controversy has developed concerning the orientation of the dicarbon fragments with respect to their metal neighbors. A structure of pentagonal dodecahedron, corresponding to a cage with T_h symmetry, was initially proposed to explain the special

stability of the Ti$_8$C$_{12}$ cluster by a structural analogy with the hypothetic C$_{20}$ fullerene.[1] This structure can also be seen as a cube of metal atoms with each face capped by a dicarbon fragment parallel to two of its edges (Figure 1A). It soon appeared that this structure with T_h symmetry is not compatible, at least for titanium, with a low-spin description of the neutral cluster.[4e] Hay[5] then showed that the electronic configuration with lowest energy for the T_h cage of Ti$_8$C$_{12}$ corresponds to a nonet state (^{9}A$_g$) with the eight unpaired electrons localized each on a different titanium atom. Then, geometrical optimization processes carried out, using either the Density Functional

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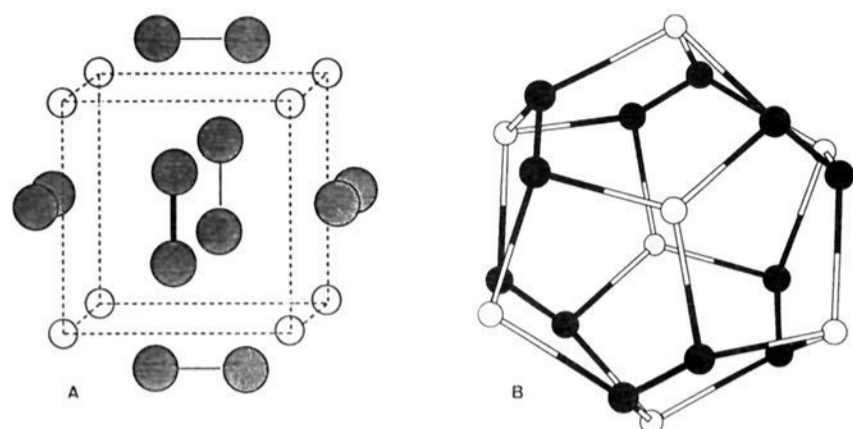(12) Emsley, J. *New Scientist* **1992**, April 11, 16.

Figure 1. Two views of the Ti_8C_{12} cluster in the cage structure of pentagonal dodecahedron. The structure at the right-hand side (d_{C-C} = 1.375 Å, d_{Ti-C} = 2.128 Å) corresponds to the optimal geometry associated with the ^9A_g state,[5] assuming the constraints of the T_h symmetry.

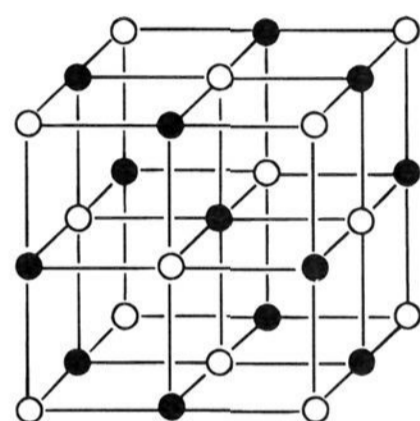**Figure 2.** Structures of $3 \times 3 \times 3$ fcc crystallite assumed for $Ti_{14}C_{13}$.

approach or the ab initio Hartree—Fock methodology, have shown that a 45° rotation of all dicarbon fragments with respect to the underlying skeleton of metal atoms was leading to cage structures with 36 metal—carbon bonds seemingly much more stable than the pentagonal dodecahedron.[6-10]

Mass spectrometer investigation on the titanium—carbon and vanadium—carbon clusters has also been going on. Pilgrim and Duncan[13] have reported "large peaks" occurring not only for $M_8C_{12}{}^+$ clusters, but also for larger metal—carbon species exhibiting 1:1 M/C stoichiometries. More specifically, "super magic" peaks similar to those obtained for M_8C_{12} were characterized for $Ti_{14}C_{13}{}^+$ and $V_{14}C_{13}{}^+$, suggesting for those species a $3 \times 3 \times 3$ cubic structure (Figure 2).[13] Magic peaks corresponding to the same stoichiometry were detected under specific experimental conditions with niobium[14a] and with tantalum.[14b] The goal of the present paper is then an analysis of the electronic and geometric structures of the Ti_8C_{12} cluster, focused on the characterization of the various minima of the potential hypersurface and on the importance of electron correlation for a quantitative estimate of their relative energies. After the work of Reddy and Khanna, carried out using the density functional methodology,[11] we will also present an ab initio SCF investigation of the $Ti_{14}C_{13}$ crystallite, including a complete geometry optimization and an analysis of the bonding in the nanocrystals compared to that of metallocarbohedrenes.

II. Computational Details

The seven structures corresponding to local minima on the potential hypersurface of Ti_8C_{12} have been obtained by means of gradient optimization at the one-configuration Hartree—Fock level, using the TURBOMOLE program.[15] The geometry optimization of the $Ti_{14}C_{13}$ crystallite in the O_h and T_d symmetry

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Table 1. Interatomic Distances (Å) Optimized at the One-Configuration SCF Level for the Topologically Notable Points Characterized on the Potential Energy Surfaces of Ti_8C_{12} and $Ti_{14}C_{13}$

symmetry	state	C—C	Ti—C (end-on)	Ti—C (side-on)	Ti—Ti
		Ti_8C_{12}			
T_h	^9A_g	1.375	2.128		3.309
		$(1.346)^a$	$(2.070)^a$		$(3.269)^a$
		$(1.40)^b$	$(1.98)^b$		$(3.06)^b$
		$(1.40)^c$	$(1.99)^c$		$(3.02)^c$
T_d	$^5A_2$	1.343	1.964	2.265	3.114
		$(1.34)^c$	$(1.93)^c$	$(2.19)^c$	$(2.86)^c$
					2.943
					$(2.90)^c$
D_{2d}	$^1A_1$	1.259	2.104	2.253	3.116
		$(1.36)^d$	$(1.95)^d$	$(2.08)^d$	$(2.77)^d$
		1.343	2.345	2.393	3.243
		$(1.37)^d$	$(2.04)^d$	$(2.09)^d$	$(2.81)^d$
				2.585	
D_{3d}	$^1A_{1g}$	1.285	2.070	2.382	3.121
			2.271	2.418	3.203
D_{3d}	$^1A_{1g}$	1.323	2.020	2.189	2.706
				2.292	2.794
					2.945
					3.268
D_2	^1A	1.261	2.149	2.278	3.088
		1.294	2.239	2.317	3.245
			2.308	2.346	3.260
				2.391	3.273
				2.420	
				2.582	
C_{2v}	$^1A_1$	1.289	1.837	2.249	2.863
		1.421	1.846	2.257	2.965
		1.446	2.057	2.275	3.022
			2.250	2.319	3.071
				2.406	3.181
				2.451	3.432
C_s	$^1A'$	1.256	1.852	2.170	2.997
		1.259	2.105	2.250	3.020
		1.308	2.203	2.254	3.099
		1.467	2.239	2.284	3.128
			2.244	2.341	3.241
			2.268	2.402	3.272
			2.344	2.409	3.572
				2.445	
				2.504	
				2.546	
				2.567	
				2.616	
		$Ti_{14}C_{13}$			
O_h	$^5A_{2g}$		2.029		2.865
			2.107		2.980
			2.111		
			$(2.04)^c$		
T_d	$^5A_2$		1.992		2.808
			2.068		2.924
			2.107		2.980
			2.117		

[a] Reference 5. [b] Reference 4a. [c] Reference 6. [d] Reference 7. [e] Reference 11.

groups was carried out by means of the ASTERIX program system.[16] The geometries are displayed in Table 1. The same atomic basis sets were used for both molecules. The Gaussian basis set used for titanium is a (13s, 8p, 5d) set obtained by

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adding one p function of exponent 0.15 to the set optimized by Hyla—Kryspin et al.[17] It was contracted into (5, 3, 3). The basis set used for carbon is a (9s, 5p) set taken from Huzinaga[18] and contracted into (3, 2). The molecular basis sets are then made of 824 Gaussian functions for Ti_8C_{12} and 1250 such functions for $Ti_{14}C_{13}$, respectively, yielding 364 and 565 contracted orbitals. The CI expansions carried out on Ti_8C_{12} and the coupling of the four electrons localized on metal atoms on $Ti_{14}C_{13}$ were performed by using Siegbahn's contracted CI program.[19]

III. Ti_8C_{12}: Cluster with T_d Symmetry and 36 Metal—Carbon Bonds. One-Configuration Hartree—Fock Results

1. Requirement for d-Electron Localization. The determination of the preferred structure of M_8C_{12} clusters is a tricky problem for at least three reasons: (1) the seemingly large number of local minima that can be characterized on the potential energy hypersurface at the one-configuration HF level;[8] (2) the difficult guess of the electronic configuration with lowest energy that should be associated with a given molecular topology (the characterization by Hay of a nonet ground state for the structure of pentagonal dodecahedron[5] is a striking example of that problem); and (3) the problem of the symmetry-imposed delocalization of the metal d electrons that may alter the results obtained at the one-configuration HF level. Let us illustrate those problems by the case of the cage structure with T_d symmetry which is expected from the present study and from others[6,9,10,20] to be the most stable conformation for Ti_8C_{12}.

Dance[6] was first to show from density functional calculations that relaxing the symmetry constraints of the T_h point group induces a considerable decrease of the energy ($\sim$350 kcal mol^{-1}) in relation with an important change in the molecular topology. The structure optimized by Dance exhibits T_d symmetry and can be described as a tetracapped tetrahedron of metal atoms bridged by the six C_2 fragments. A closer look to this structure shows that it can be deduced from the pentagonal dodecahedron by a $\pm 45°$ rotation of the opposite C_2 units together with a butterfly folding of each face of the Ti_8 cube (Figure 5A). While the four capping metal atoms are σ-coordinated each to the three adjacent C_2 units, the "inner" Ti atoms are surrounded each in a nearly planar conformation by six carbons displaying side-on coordination.

The electronic structure of the tetracapped tetrahedral clusters of M_8C_{12} was recently interpreted by Lin and Hall[9] on the basis of an orbital interaction diagram between the d orbital sets belonging to the "inner" and to the "outer" tetrahedral moieties. The six C_2 units were assimilated to acetylene-like dianions. On the one hand, each metal atom of the inner tetrahedron is bonded to the three surrounding, side-on coordinated C_2 units by means of π donation involving the $d_{x^2-y^2}$ and d_{xy} orbitals, assuming the z axis to be perpendicular to the plane of coordination. On the other hand, each capping metal atom is σ-coordinated to three acetylene ends in a pyramidal arrangement. Once again, two orbitals per metal atom are involved in bonding, and the t_{2g} triad of the ML_3 fragment is left available

for metal—metal interaction. To summarize, two d orbitals per metal atom play the role of acceptor to form metal—carbon bonds with either the π bonding orbitals of the acetylene-like units (for the metal atoms of the inner tetrahedron, hereafter referred to as *thn*) or the σ lone pairs of the same $(C_2)^{2-}$ (for the metal atoms of the outer tetrahedron **THN**). From the 20 d-type levels generated by each tetrahedron of metal atoms, 12 therefore remain available to accommodate the metal electrons. As evidenced by the orbital diagram of Lin and Hall (Figure 1 in ref 9), those 12 levels belong to the irreducible representations $a_1 + t_2 + e + t_1 + t_2$, in that order. Those levels remain clustered in **THN**, but undergo a significant scattering in *thn* due to metal—metal interaction.[21] When those two sets of 12 levels are allowed to interact, they give rise to three groups of molecular orbitals. The lowest group, $1a_1 < 1t_2 < 1e < 1t_1$, is composed of nine MOs which are stabilized by the metal—metal interactions. Then comes a second group of 12 levels ($2a_1 < 2t_2 < 3t_2 < 2e$), slightly antibonding. *Each of those orbitals is delocalized throughout the metal backbone according to the constraints of the T_d point group.* Since each acetylene-like unit has a formal charge of 2$-$, the metal backbone should be globally attributed a 12+ charge, and the number of d electrons to be accommodated on the metal orbitals is 20 for M = Ti or Zr. Relying on the aufbau principle, Lin and Hall suggest that 18 electrons will occupy the set of nine stabilized orbitals, whereas the two extra electrons would be accommodated in the lowest orbital of the slightly antibonding set, $2a_1$.[9]

Our calculations indicate that the corresponding configuration, $1a_1^2 1t_2^6 1e^4 1t_1^6 2a_1^2$, is not the most stable one (Table 2). The reason for that is the symmetry-imposed delocalization of the d electrons, and more specifically the delocalization occurring through the two in-phase combinations $1a_1$ and $2a_1$ of the metal d_{z^2}-like orbitals oriented along the four C_3 axes of the molecule. Orbital $1a_1$, mainly centered on the four vertices of the inner tetrahedron, exhibits an important bonding overlap between the in-phase atomic orbitals. Orbital $2a_1$ is the equivalent combination involving the four vertices of **THN**. It is practically nonbonding because of the larger interatomic distances (4.84 Å instead of 3.11 Å in *thn*). The other, out-of-phase combinations of the same d_{z^2}-like orbitals are the triply degenerate levels referred to as $2t_2$ and $3t_2$ in the diagram of Lin and Hall. Those levels belong to the intermediate set of slightly destabilized MOs and should remain unoccupied in application of the aufbau principle. Then, in the closed-shell configuration of Ti_8C_{12} based upon the sequence of molecular orbitals, the four metal electrons accommodated in molecular orbitals $1a_1$ and $2a_1$ are uniformly distributed among the eight metal atoms.

Single electrons dislike being shared by symmetry among equivalent centers, especially when they are accommodated on molecular orbitals that are relatively deep in energy.[22,23] A classical example consists in the description of core hole states in symmetric molecules, which may be erroneous by several tens of electronvolts if a symmetry-adapted formalism is used.[24]

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(20) Other types of cage structures have been investigated by means of ab initio[9,11] or semiempirical[4i] methods. None of them seems to be competitive with the structures exhibiting 36 metal—carbon bonds.

(21) The diagram by Lin and Hall is based on ab initio calculations carried out on Mo_8C_{12}.[9] The d—d interactions are expected to be more important for molybdenum than for titanium.

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Table 2. Total Energies (hartrees) Obtained at Various Levels of Calculation for the Notable Points of the Energy Hypersurfaces of Ti_8C_{12} and $Ti_{14}C_{13}$

symmetry	state	SCF[a]	coupling[b]	CI[c]
		Ti_8C_{12}[d]		
T_h	^9A_g[e]	−0.089 49		
T_d	$^5A_2$[f]	−0.392 40		−0.732 34
	$^3T_1$		−0.399 44	−0.742 48
	$^1A_1$		−0.402 67	−0.749 17
T_d	$^5A_2$[g]	−0.226 87		
	$^1A_1$[g]		−0.226 28	−0.546 13
T_d	$^1A_1$[h]	−0.120 20		
T_d	$^9A_1$[i]	−0.261 47		
D_{2d}	$^1A_1$	−0.335 80		−0.501 40
D_{3d}	$^1A_{1g}$	−0.261 18		−0.495 67
D_{3d}	$^1A_{1g}$	−0.077 66		−0.496 78
D_2	^1A	−0.279 63		−0.498 87
C_{2v}	$^1A_1$	−0.199 90		−0.506 11
C_s	$^1A'$	−0.232 27		−0.463 35
		$Ti_{14}C_{13}$[j]		
O_h	$^5A_{2g}$	−0.147 23		
T_d	$^5A_2$[f]	−0.168 15		
	$^1A_1$		−0.168 18	
	$^5A_2$[g]	−0.087 48		

[a] One-configuration Hartree—Fock; geometry optimized for the state of lowest energy in each symmetry. [b] Triplet or singlet coupling of the four unpaired electrons. [c] Correlation of the 20 electrons formally attributed to the titanium atoms, including the four unpaired electrons in the T_d form. [d] All energies shifted by −7228 hartrees. [e] Electronic configuration proposed in ref 5 for the structure of pentagonal dodecahedron. [f] Ground state, optimal geometry. For Ti_8C_{12}, the unpaired electrons are localized on the small tetrahedron of metal atoms. [g] Excited state, geometry optimized for the quintet ground state. For Ti_8C_{12}, the unpaired electrons are localized on the large tetrahedron of metal atoms. [h] Closed-shell configuration based upon the aufbau principle and assuming the orbital ordering of ref 9. Geometry optimized for the quintet ground state. [i] Nonet state equivalent to that proposed by Hay[5] to be the ground state of the T_h form. Geometry optimized for the quintet ground state. [j] All energies shifted by −12 347 hartrees.

The electrons of transition metal d shells, and particularly those of the 3d shell in the first transition series, exhibit a similar, though less dramatic behavior.[25] Problems arise, for instance, in the symmetry-adapted description of ionized states in dimetallic molecules.[26] The present case is an extension of the same problem to a more complex architecture made of two sets of four equivalent metals. As a result, orbitals $1a_1$ and $2a_1$ are artificially shifted up in energy, especially the latter one (e_{2a1} = −0.124 hartree): The total energy associated with this closed-shell configuration is −7 228.120 20 hartrees (Table 2).

Let us now reconsider the problem by taking care of electron relocalization. The four electrons previously accommodated on orbitals $1a_1$ and $2a_1$ should be relocalized on specific metal centers. Two solutions are possible without destroying symmetry adaptation. The first possibility consists in localizing the four electrons on the four equivalent atoms of the *inner tetrahedron*. This should be obtained by equally populating the four combinations of the corresponding d_{z^2}-like atomic orbitals, namely, $1a_1$ and $2t_2$. We end up with an open-shell quintet configuration $^5A_2$ associated with the electron distribution $1t_2^6 1e^4 1t_1^6 1a_1^2 2t_2^3$, and a total energy equal to −7 228.392 47 hartrees. This configuration was found to be lowest in energy

(25) (a) Newton, M. D. *Chem. Phys. Lett.* **1982**, *90*, 291. (b) Cox, P. A.; Bénard, M.; Veillard, A. *Ibid.* **1982**, *87*, 159. (c) Messmer, R. P.; Caves, T. C.; Kao, C. M. *Ibid.* **1982**, *90*, 296. (d) Post, D.; Baerends, E.-J. *Ibid.* **1982**, *86*, 176. (e) Bénard, M. *Ibid.* **1983**, *96*, 183.

(26) (a) Van Dam, H.; Oskam, A. *Transition Metal Chemistry*; Melson, G. A., Figgis, B. A., Eds.; Marcel Dekker: New-York, 1985; Vol. 9, pp 125–308. (b) Granozzi, G.; Mougenot, P.; Demuynck, J.; Bénard, M. *Inorg. Chem.* **1987**, *26*, 2588. (c) Quelch, G. E.; Hillier, I. H. *Chem. Phys. Lett.* **1988**, *144*, 153. (d) Clark, D. L.; Green, J. C.; Redfern, C. N.; Quelch, G. E.; Hillier, I. H. *Chem. Phys. Lett.* **1989**, *154*, 326.

at the one-configuration RHF level, and the value obtained for the total energy results from gradient optimization of the geometry. This optimal geometry has been used for all calculations subsequently carried out on other electronic configurations.

The second solution requires the location of the four electrons on the four equivalent atoms of the *outer tetrahedron*. In this case, the four molecular orbitals to be equally populated are $2a_1$ and $3t_2$. Another open-shell quintet configuration with same A_2 symmetry is obtained, but the total energy is now −7 228.226 87 hartrees, that is, 104 kcal mol^{-1} higher than the ground-state energy (Table 2). At least part of this energy difference should be assigned to the metal—metal interactions, which stabilize $1a_1$ and somewhat raise the energy of $2a_1$. The nature of metal—carbon interactions is also at work, as will be seen in the next section.

2. Ti_8C_{12}: A Mixed-Valence Cluster? Let us now consider in more detail the electronic structures associated with each of those two states. Remember first that the six C_2 units are formally $(C_2)^{2-}$, which settles to 20 the number of d metal electrons. The formal distribution of those 20 electrons appears quite different in the two quintet states. In the quintet ground state, each of the eight doubly occupied orbitals with major metal character is localized mainly on the four titanium atoms of the *large tetrahedron* (**THN**) with weights varying from 37.5 to 41%. The weights on the remaining metal atoms range from 25.5 to 31.5%. This preeminence of the large tetrahedron, as far as the set of metal valence orbitals is concerned, should be recognized by formally attributing 16 electrons to the set of metal atoms belonging to **THN**. Those atoms are therefore assigned the electronic configuration d^4, corresponding to the ionization state Ti(0). Back-donation interactions are effective toward the π^* orbitals of the acetylene-like dicarbons. The four remaining d electrons are localized at 97% on the *small tetrahedron* (*thn*) of metal atoms, and accommodated on four d_{z^2}-like orbitals with lobes oriented along the appropriate C_3 axis of the tetrahedron. Those four electrons are weakly coupled and give rise to the quintet state. The Ti atoms of *thn* then correspond to the formal electronic configuration d^1 and to the ionization state Ti(III).[27]

Considering now, for the same geometry, the excited quintet state, 104 kcal mol^{-1} above the ground state, we find the opposite distribution of the 20 electrons among the 8 metal atoms. The four weakly coupled electrons giving rise to the quintet state are now localized on **THN**, and still accommodated in d_{z^2}-like orbital combinations. The metal atoms of **THN** are then formally Ti(III), corresponding to a d^1 electronic configuration. Conversely, all of the eight occupied metal orbitals have their major weights (47 to 50.5%) on the metal atoms of *thn*, with smaller contributions (19.5 to 25%) from the remaining metal atoms. The metal atoms of *thn* then formally become d^4 and the metal d_{z^2}, d_{xz}, and d_{yz} orbitals behave as donors toward the π^* orbitals of the side-on coordinated C_2 units. The transition from the ground-state quintet to the excited-state quintet could be symbolized as follows:

$$Ti_4(0)_{THN}Ti_4(III)_{thn} \rightarrow Ti_4(III)_{THN}Ti_4(0)_{thn} [28]$$
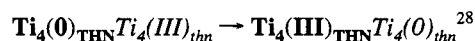
The characterization of those quintet states corresponding to

(27) Because of the complex interplay of counter-polarizations and metal—carbon interactions, this formal assignment of the d metal populations is clearly visible neither from the Mulliken point charges, nor from the d metal populations. Those populations are nearly identical (2.62e and 2.61e) for both types of metal atoms in the ground-state configuration. In the excited quintet configuration, however, the metal d populations are 2.72e and 2.43e for the metal atoms belonging to *thn* and **THN**, respectively. In spite of its limited scale, this shift of the d populations is in agreement with the proposed exchange of the formal oxidation numbers.
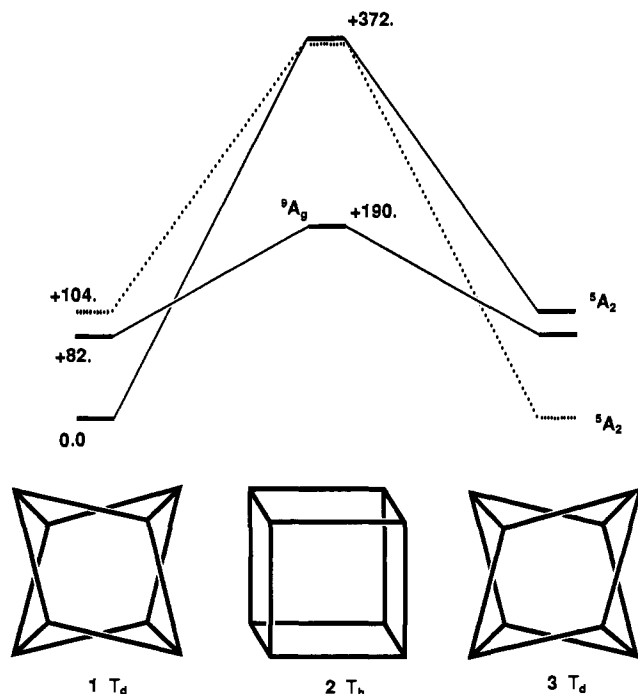
Figure 3. Ti$_8$C$_{12}$: Energy path computed for a hypothetic interconversion of the two Ti$_4$ tetrahedra of the T_d form through an intermediate structure with T_h symmetry. The C$_2$ units have been omitted for clarity (relative energies in kcal mol^{-1}).

distinct schemes for the distribution of the d electrons between both sets of metal atoms is reminiscent of mixed-valence clusters.[29] In such a case the transition from the quintet state of lowest energy to the excited quintet with opposite localization scheme could be assimilated to the intervalence absorption (Figure 3). According to the standard theory of mixed-valence complexes,[30] a pathway involving an avoided crossing should be found between the excited quintet state of conformation **1** and the quintet ground state of its mirror image **3** (Figure 3). The geometry of the cage cluster intermediate between **1** and **3** precisely corresponds to the structure of pentagonal dodecahedron with T_h symmetry (**2**, Figure 3). The quintet state

correlating with the ground state of **1** and with the excited state of **3** has been characterized for conformation **2** under the constraints of the largest symmetry subgroup common to T_d and to T_h, namely, point group T. The quintet state characterized in such conditions for conformation **2** can therefore be considered as a broken-symmetry solution.[23] The coupling between the degenerate, nonorthogonal terms of this quintet state has not been estimated. In spite of a nonvanishing through-space overlap between the d$_{z^2}$-like orbitals centered on the various metal atoms, the J coupling term[31] can be considered as negligible in regard to the energy differences obtained with respect to the ground and excited quintet states of the conformation with T_d symmetry.

To our surprise, indeed, the SCF energy computed for the doubly degenerate quintet state of **2**,[32] −7227.7988 hartrees, is considerably higher than both the ground and the excited states of **1** and **3** (Figure 3). The destabilization amounts to 372 kcal mol^{-1} with respect to the ground state and 269 kcal mol^{-1} with respect to the excited state. This large barrier is attributable to the titanium−carbon interactions being less favorable in **2**. In **1** and **3**, each dicarbon unit is part of a planar, acetylene-like
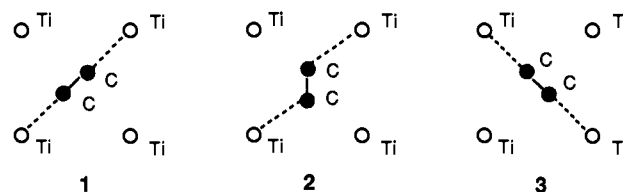
Ti−C≡C−Ti structure stabilized through interactions involving the π and especially the π^* orbitals. This electronic structure typical of acetylene molecules is retained in the quintet state of **2**, even though the Ti−C≡C−Ti skeleton is not planar anymore, and best suited to an *ethylenic* structure involving the two other cofacial Ti atoms:[33]
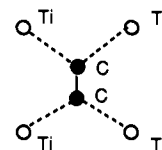
Such an ethylenic structure with three Ti−C bonding orbitals on each of the eight metal atoms is achieved in the ^{9}A$_g$ state first characterized by Hay,[5] and corresponding to the ground state of **2**. After a gradient optimization of the geometry, this nonet state was characterized at −7228.0895 hartrees, that is, at +190 kcal mol^{-1} with respect to the ground state of **1**. Hay specifies that the 30 σ-bonding orbitals of the system, including the six C−C bonds, transform according to the T_h group as 2a$_g$ + 1a$_u$ + 2e$_g$ + 1e$_u$ + 3t$_g$ + 4t$_u$. One of those levels, 1a$_u$, however, appears from the present calculations to be a rather unstable combination (e = −0.143 hartree) mainly based upon metal 4s atomic orbitals. As a consequence, the nonet ground state of **2** is *unstable* with respect to a deformation of the molecular framework along the T symmetry. The total energy

(28) A referee found this interpretation questionable since it is difficult to believe that the difference between the ground and the excited quintet states involves all eight Ti atoms changing oxidation states by 3 units. As stated in the above footnote, the only consideration of the global point charges on the metal atoms could lead to the conclusion that the differences between (i) the two metal sites and (ii) the two quintet states are relatively minor from the viewpoint of the charge density. An analysis of the *distribution* of this density completely reverses this picture. The most prominent change involves the four unpaired electrons accommodated in d$_{z^2}$-like orbitals. An excitation from the ground to the excited quintet, or singlet-coupled, states implies a transfer of those electrons from *thn* to **THN**, and this transfer is complete. The case of the 16 other d metal electrons is more ambiguous. The distribution between *thn* and **THN** of the. d metal electrons accommodated in the eight doubly occupied metal MOs displays changes of much smaller amplitude, since the weight of those metal electrons localized on either tetrahedron is typically varying from 25% to 40 or 50% and vice-versa (see text). A possible interpretation would consist of attributing those fluctuations to a counter-polarization effect induced by the transfer of the four unpaired electrons from one tetrahedron to the other. The excitation to the high-energy state would then require each Ti atom to change its oxidation state by only one unit. This approach, however, does not account for the qualitative change which makes *all* doubly occupied metal orbitals to be mainly localized on **THN** in the quintet (or singlet coupled) state of low energy, and on *thn* in the excited state of same spin multiplicity. For this reason, the more dramatic interpretation proposed in the text has been preferred, even though the assignment of formal oxidation states, in the present case as in others, is not devoid of ambiguity.

(29) (a) Borshch, S. A.; Bominaar, E. L.; Blondin, G.; Girerd, J.-J. *J. Am. Chem. Soc.* **1993**, *115*, 5155. (b) Marks, A. J.; Prassides, K. *Chem. Phys.* **1994**, *179*, 93 and references therein.

(30) *Mixed-Valence Compounds* (NATO ACS Series C, Vol. 58); Brown, D. B., Ed.; D. Reidel: Dordrecht, Holland, 1980.

(31) Hush, N. S., ref 30, pp 151−188.

(32) The geometry used for **2** was the one optimized for the ^{9}A$_g$ configuration described by Hay.[5]

(33) The acetylenic quintet configuration obtained for the structure of pentagonal dodecahedron **2** is, in fact, doubly degenerate, since the dicarbon fragments can be σ-bonded to either couple of metal atoms of the underlying face. One of those degenerate electronic configurations correlates with the low-energy quintet associated with geometrical conformation **3**, whereas the other one leads back to its mirror image, conformation **1**. On the other side of the energy surface, the degenerate quintet states of **2** are expected to correlate with high-energy quintets of **1** and **3** (not characterized in the present work) in which each C$_2$ fragment is σ-bonded to the *alternate* pair of underlying metal atoms.
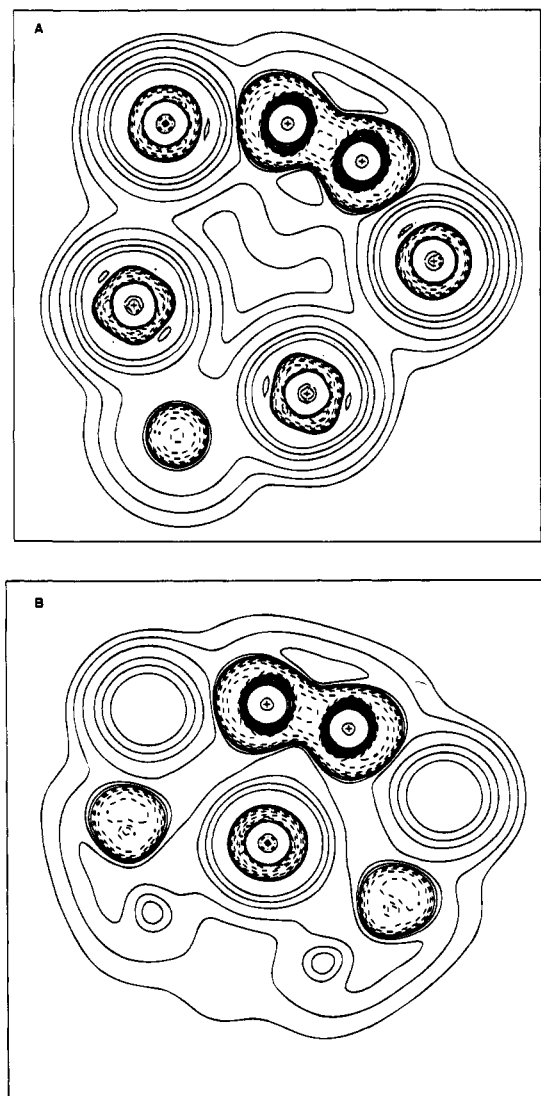
Figure 4. Plots of $\nabla^2\varrho$ for Ti_8C_{12} in the optimal conformation with T_d symmetry, $^1A_1$ ground state, CI wave function: (A) plane containing one C_2 unit and two σ-bonded Ti atoms belonging to the large tetrahedron, **THN**; (B) plane containing one C_2 unit and one π-bonded Ti atom belonging to the small tetrahedron, *thn*. Solid lines for $\nabla^2\varrho$ > 0 (regions of charge depletion); broken lines for $\nabla^2\varrho$ < 0 (regions of charge concentration).

found for the nonet state in conformation **1** is $-7228.261\ 47$ hartrees, lower by 108 kcal mol^{-1} than the equivalent state in conformation **2** (Figure 3).

3. Laplacian Distribution of the Charge Density in the Cage Structures of Ti_8C_{12} with T_d and T_h Symmetries. It has been shown that the Laplacian function of the total density displays the shell structure of atoms, therefore allowing discussion of the reorganization of the valence shell induced by chemical bonding.[34] The Laplacian distribution of the charge density has been analyzed first for Ti_8C_{12} in its conformation with T_d symmetry. The charge density was generated from the wave function computed at the CI level for the ground state of the T_d form, corresponding to a singlet coupling of the four unpaired electrons (section IV and Table 2). Figure 4A represents the Laplacian function in a plane containing one C_2

unit σ-bonded to two metal atoms of **THN**, whereas Figure 4B illustrates the π interaction between a C_2 group and a metal atom of the small tetrahedron *thn*. Broken lines are characteristic of local concentrations of charge density. Both figures clearly display a cylindric shape for the electron distribution in the vicinity of the carbon atoms. This cylindric deformation of the Laplacian distribution corroborates the acetylenic character of the C_2 fragment.[35]

Each carbon atom displays a local maximum in charge concentration (maximum in $-\nabla^2\varrho$, referred to as a (3, -3) critical point in the topological analysis of the Laplacian distribution) located along the Ti$-$C σ bond (Figure 4A). Along the same Ti$-$C bond axis, but on the metal side, is found a local *minimum* in $-\nabla^2\varrho$, or (3, $+3$) critical point corresponding to a depletion of charge concentration. This distribution of $\nabla^2\varrho$, with a (3, -3) critical point on the ligand side and a (3, $+3$) cp on the metal side, is characteristic of σ-donation.[36]

In Figure 4B, the charge distributions in the carbon atoms are governed by the bonding between Ti$_{thn}$ and the two carbon atoms. The π nature of this coupling is illustrated by the deformation of the charge density along C_2 toward the metal center. The integration of the electron density over the domain defined by the surfaces of zero gradient flux[37] provides for the C_2 units a net charge of $-2.05e$, larger than the Mulliken charge ($-1.33e$) and very close to the formal charge of $-2e$ assumed for the acetylenic C_2.

An analysis of the Laplacian function has also been carried out for the density distribution generated by the structure with T_h symmetry in its ^9A_g ground state. The ethylenic character of the C_2 unit in that conformation is confirmed by the appearance of two (3, -3) critical points around each carbon, approximately oriented toward the nearest metal neighbors.

IV. Ti_8C_{12}: Secondary Minima on the Potential Hypersurface and the Effect of Correlation

1. The Seven Minima: SCF and CI Energies. Gradient optimization processes carried out on Ti_8C_{12} do not necessarily converge toward structure **1** when they are not constrained by symmetry. Other attractors do exist on the potential hypersurface. Some were characterized by chance such as the structures with D_{3d} and with C_{2v} symmetry respectively represented in Figure 5, D and F,[8] or the cage with D_{2d} symmetry (Figure 5B) proposed by Chen et al.[7] to be the ground state. Those cages, and also structure **1** with T_d symmetry, share a common character: they can be described as distorted cubes of metal atoms with a C_2 unit capping each face *along one diagonal*. Each of those cages gives rise to 36 metal$-$carbon distances within bonding range. It was inferred[8] that all structures with 36 metal$-$carbon bonds could correspond to energy minima. The requirement for 36 M$-$C bonds implies that each C_2 unit should be oriented along one or the other diagonal of the underlying face of the pseudo-cubic framework. This gives rise to a maximal number of $2^6 = 64$ conformations, seven of them being topologically distinct. Gradient optimization has been carried out at the one-determinant SCF level for all seven forms, assuming a closed-shell singlet conformation for all of them except for the one with T_d symmetry (**1**). As expected, local minima have been characterized for all distinct

(34) (a) Bader, R. F. W.; Essén, H. *J. Chem. Phys.* **1984**, *80*, 1943. (b) Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* **1984**, *106*, 1594. (c) Bader, R. F. W.; Gillespie, R. J.; MacDougall, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7329. (d) MacDougall, P. J.; Hall, M. B.; Bader, R. F. W.; Cheeseman, J. R. *Can. J. Chem.* **1989**, *67*, 1842.
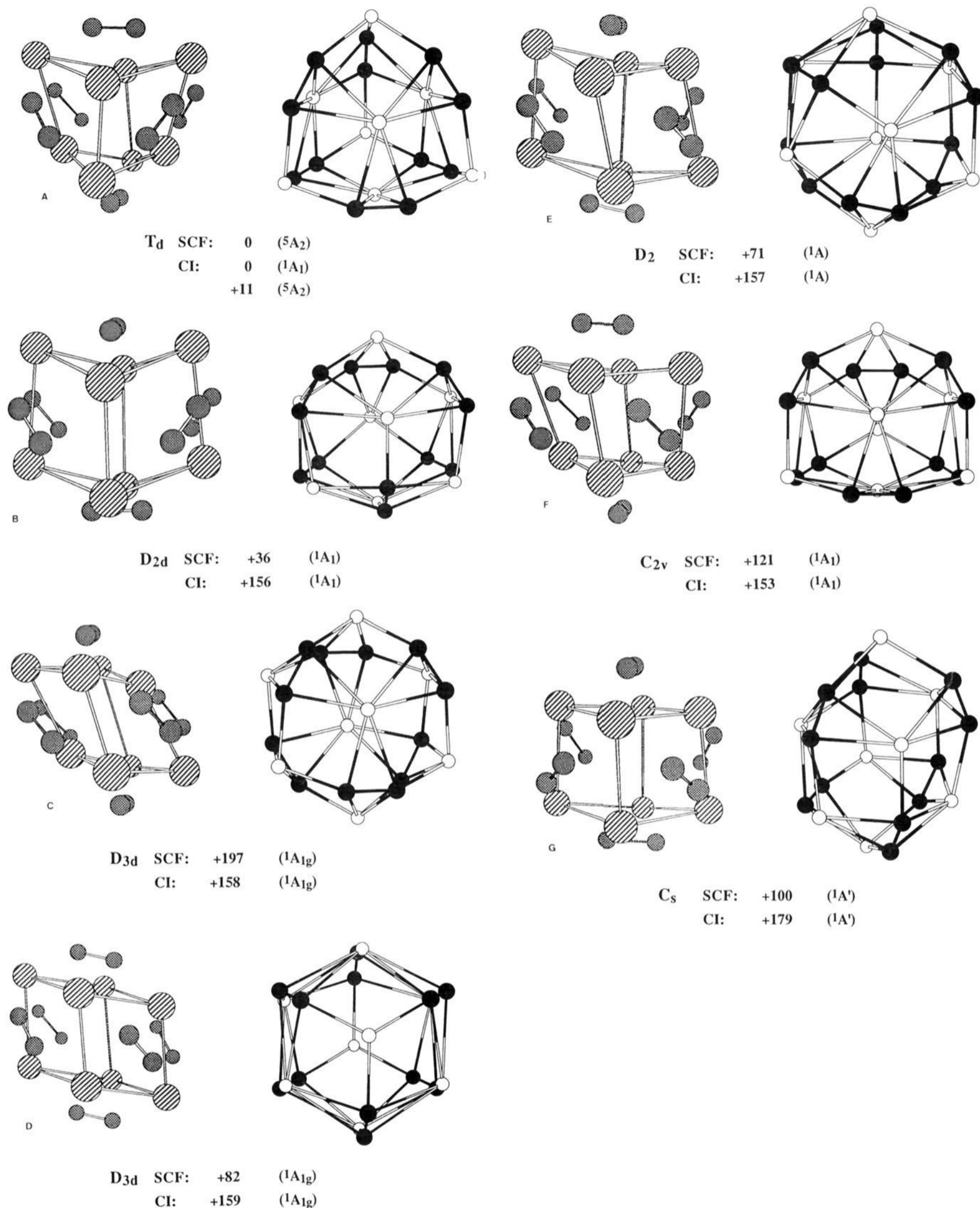
(35) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061.

(36) (a) Bo, C.; Sarasa, J.-P.; Poblet, J.-M. *J. Phys. Chem.* **1993**, *97*, 6362. (b) Bo, C.; Poblet, J.-M.; Bénard, M. *Chem. Phys. Lett.* **1990**, *169*, 89. (c) Costas, M.; Poblet, J.-M.; Rohmer, M.-M.; Bénard, M. *Inorg. Chem.*, in press.

(37) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63.

T_d	SCF:	0	($^5A_2$)
	CI:	0	($^1A_1$)
		+11	($^5A_2$)

D_2	SCF:	+71	(^1A)
	CI:	+157	(^1A)

D_{2d}	SCF:	+36	($^1A_1$)
	CI:	+156	($^1A_1$)

C_{2v}	SCF:	+121	($^1A_1$)
	CI:	+153	($^1A_1$)

D_{3d}	SCF:	+197	($^1A_{1g}$)
	CI:	+158	($^1A_{1g}$)

C_s	SCF:	+100	($^1A'$)
	CI:	+179	($^1A'$)

D_{3d}	SCF:	+82	($^1A_{1g}$)
	CI:	+159	($^1A_{1g}$)

Figure 5. SCF optimized geometries of the seven minima characterized on the potential energy hypersurface of Ti_8C_{12} (relative energies in kcal mol^{-1}).

topological structures. The interatomic distances are displayed in Table 1, and the corresponding cluster shapes are represented in Figure 5, together with their relative energies computed at the one-configuration SCF, and at the configuration interaction levels. The conformation with tetrahedral symmetry is lowest in energy at both levels of calculation. The relative SCF energies optimized for the six other structures are scattered between +35.6 kcal mol^{-1} (D_{2d} structure, Figure 5B) and +197.5 kcal mol^{-1} (D_{3d} structure, Figure 5C).[38] We expected those energy values to suffer an important bias due to the artificial delocalization of the d electrons induced by the

(38) The energy of conformation C with D_{3d} symmetry, was erroneously shifted up in ref 8 by 0.1 hartree, yielding a relative energy of +259.2 kcal mol^{-1} with respect to the T_d ground state, instead of +197.5 kcal mol^{-1}.

symmetry constraints. Since those artifacts can be at least partly corrected by properly accounting for nondynamic correlation, CI expansions designed to correlate the 20 metal valence electrons were carried out starting from the wave functions optimized at the SCF level. A special, multireference treatment was designed for the cluster with T_d symmetry in order to consider a singlet coupling of the four unpaired metal electrons (see section IV.2). This $^1A_1$ state was found lower than the quintet $^5A_2$ state by 6.5 kcal mol^{-1} when the CI expansion is restricted to the four metal electrons, and to 10.5 kcal mol^{-1} when all 20 metal valence electrons are correlated. The total energy corresponding to the singlet state at that level of calculation is $-7228.749\ 17$ hartrees (Table 2), which is taken in Figure 5 as the reference energy for CI calculations.

The CI energies associated with all secondary minima are clustered at about $+160$ kcal mol^{-1} with respect to the energy of the T_d form. We attribute the distinctive stability of the T_d structure to the specific arrangement of the C_2 ligands which fully separates the σ interactions involving the large tetrahedron of metal atoms from the π interactions concentrated into the small tetrahedron. Such a separation, allowing for the high-spin conformation of **1** and for its formal description in terms of a mixed-valence cluster, does not exist in the other structures in which most metal atoms concurrently take part in σ and π interactions. An important proportion of the C—C distances optimized in those secondary minima are shorter than 1.30 Å (Table 1), suggesting that the metal—carbon interactions involving the π^* orbitals of the C_2 fragments are not so efficient as in the T_d form.

2. The T_d Conformation: Analysis of the CI Expansions. Let us now discuss the nature of the CI wave functions obtained for the quintet state of lowest energy and for the ground and the excited singlet-coupled states of the conformation with T_d symmetry. Correlating the 16 d electrons accommodated in closed shells lowers the energy by about one-third of a hartree (Table 2). The CI expansion obtained for the lowest quintet state is typical of a state with no more than one leading configuration. The coefficient of the reference state is 0.898, and no other coefficient is above 0.05. This implies that the leading configuration does not significantly interact with the other quintet configuration characterized 104 kcal mol^{-1} higher in energy, even though this interaction is allowed by symmetry (Figure 3). This should not appear surprising, since the specific electron localization schemes associated with those two configurations implies a vanishing overlap (see section III.2). The populations of the eight strongly occupied natural orbitals are comprised between 1.95 and 1.96e. The lack of any configuration with large coefficient, except for the leading one, and the similar populations of the eight strongly occupied natural orbitals suggest a uniform distribution of the correlation effects among the 16 spin-coupled metal electrons.

This conclusion is confirmed by the analysis of the CI expansion leading to the $^1A_1$ ground state when the four unpaired electrons are singlet coupled. This coupling generates a set of eight configurations with large weights which represent the reference space. The coefficient $C = (\Sigma c_i^2)^{1/2}$ associated with the reference space is 0.899, reproducing almost identically the coefficient of the leading quintet configuration in the corresponding expansion. As for the quintet expansion, no configuration external to the reference space appears with a coefficient exceeding 0.05. More specifically, the closed-shell configuration proposed by Lin and Hall to be the ground state[9] is not a significant contributor to the singlet ground state. This is not unexpected in view of its relatively high energy ($+0.27$

hartree with respect to the lowest quintet) and of the different distribution in space of the metal valence electrons.

A similar CI expansion was carried out, starting from the orbitals of the *excited* quintet state, coupling the four unpaired electrons into singlet, and correlating the complete set of 20 metal electrons. The energy of the excited singlet state was found to be $-7228.546\ 13$ hartrees (Table 2), with, again, no configuration with significant weight outside the reference space. The coefficient associated with the reference space is 0.905. The distribution of the CI coefficients and the population of the natural orbitals *inside the reference space* for both the ground and the excited singlet-coupled states provides an insight into the nature and the strength of the coupling. Remember that, in the ground state, the four electrons are localized on the small tetrahedron and distributed among the $1a_12t_2$ set of four MOs. Orbital $1a_1$ corresponds to the in-phase, bonding combination of the four d_{z^2}-like metal orbitals. The bonding interaction is strong enough in the small tetrahedron to favor in the spin coupling expansion the three reference configurations in which $1a_1$ is doubly occupied ($C = 0.69$) with respect to the three other ones in which it is unoccupied ($C = 0.39$). The high population of the $1a_1$ natural orbital, 1.40e, confirms this preeminence. In the excited quintet and singlet states, the four electrons are localized on the large tetrahedron. Owing to the long Ti—Ti distances in **THN**, the corresponding in-phase orbital $2a_1$ has little bonding character, and the coefficient associated with the reference configurations $(2a_1)^2(3t_2)^2$ ($C = 0.57$) is almost balanced by that of the reference configurations $(2a_1)^0(3t_2)^4$ ($C = 0.54$). Consistently, the population of the natural orbital corresponding to $2a_1$ is no more than 1.05e. It should also be noted in the same spirit that, contrary to what is obtained for the low energy states, the singlet coupling of the four unpaired electrons located on **THN** yields an energy which is slightly *above* the energy of the excited quintet (Table 2).

V. Ti$_{14}$C$_{13}$ Crystallite: Optimal Geometry and Electronic Structure

The structure proposed for the 27-atom cluster Ti$_{14}$C$_{13}$ detected at the mass spectrometer by Pilgrim and Duncan[13] is that of a $3 \times 3 \times 3$ fcc lattice fragment belonging to the O_h symmetry point group. A density functional investigation carried out by Reddy and Khanna assuming all Ti—C distances equal has lead to an optimal value of 2.04 Å and a binding energy of 6.7 eV/atom, compared to 6.1 eV/atom for Ti$_8$C$_{12}$ in the conformation with T_h symmetry.[11]

In the O_h structure, as in the conformation with T_d symmetry that will be considered later on, all 12 external carbon atoms are equivalent, and their environment consists of four metal atoms oriented, at least approximately, along the Cartesian axes. The geometry is fully defined with three sets of Ti—C distances, namely, (i) the six distances involving the central carbon, (ii) the 24 distances involving a metal atom in apical position, and (iii) the 24 distances between a face-centered metal and an edge-centered carbon.

An extended Hückel calculation carried out on a fragment composed of one carbon atom surrounded by its four metal nearest neighbors shows that all four valence orbitals of carbon are strongly stabilized, by 2.3 eV for the p orbitals, by 1.7 eV for the 2s orbital. The weight of carbon on the four lowest fragment orbitals is slightly less than 50% for p_x, p_y, and p_z, and 74% for 2s. The rest of the weight is equally distributed among the four metal atoms and the net charge on carbon is no more than slightly negative ($-0.43e$). This description is quite in agreement with the strong covalent bonds observed in the bulk fcc structure of titanium carbide.[39] This covalent bonding

in TiC appears compatible with intuitive electron counting which suggests that the four valence electrons of titanium are susceptible to give homopolar coupling with the four valence electrons of surrounding carbons in the fcc structure. This exact balance between valence electrons does not exist anymore in finite lattices because of the odd number of atoms. In the case of $Ti_{14}C_{13}$, there are obviously 52 valence electrons originating in carbon atoms, but 56 valence electrons are provided by titanium. In order to restore the balance, a preliminary calculation was carried out in the cation $(Ti_{14}C_{13})^{4+}$. This calculation yielded 52 molecular valence orbitals which can be expressed according to the T_d point group as $4a_1 + 1a_2 + 4e + 5t_1 + 8t_2$. Those orbitals can be correlated with the outline of covalent bonding characterized from the Ti_4C fragment, even though a certain polarity is noticed in the $Ti-C$ bonds, with important negative charges on the peripheral carbons, as on the central one.[40] Thirteen orbitals with relatively deep energy, and carbon population varying from 1.4 to 1.9 electrons can be assimilated to the carbon 2s valence orbitals. The other 39 outer valence MOs display carbon weights comprised between 0.88 and 1.53e. No more than three MOs have carbon populations less than 1 electron, and 12 outer valence MOs display carbon populations higher than 1.2e.

Where will the four remaining electrons be accommodated in the neutral cluster? It is clear, on the one hand, that those electrons originating in metal atoms cannot settle into orbital combinations delocalized over the whole cluster, since no atomic orbital of carbon remains available to build such MOs. On the other hand, no proper localization of four electrons on the Ti atoms can be considered within the constraints of the O_h point group, since the 14 metal atoms are distributed into one set of eight and one set of six atoms equivalent by symmetry. The solution most probable and straightforward consists of considering a breaking of the molecular symmetry from O_h to T_d. In such a case, the six face-centered Ti atoms remain equivalent, but the set of eight apical atoms breaks into two subsets of four, one of which is susceptible to accommodate and localize the four extra electrons. At the one-configuration SCF level, a quintet state is obtained, $5a_1^1 1a_2^2 4e^4 5t_1^6 9t_2^3$. The four electrons are accommodated as for Ti_8C_{12} in four combinations of d_{z^2}-like orbitals localized on a tetrahedron of apical titanium atoms and oriented along the C_3 axes. The geometry of the cluster has been optimized for that quintet configuration and the obtained structure is displayed in Figure 6. The $Ti-C$ distances range from 2.117 Å (face-centered Ti to edge-centered carbon) to 1.992 Å (apical titanium devoid of localized d electron to edge-centered carbon). At variance from Ti_8C_{12}, the distortion from O_h to T_d is not at all dramatic. The variations of the $Ti_{apical}-C_{edge-centered}$ distances do not exceed 0.04 Å on either side of the distance optimized under the O_h constraints, 2.029 Å. The energetical advantage of distortion also remains modest: 13 kcal mol^{-1}. At variance from met-car cages, the distortion toward a structure with T_d symmetry is not triggered by a change in the metal−carbon bonding, but only by the localization process of the four extra electrons. In that sense, $Ti_{14}C_{13}$ behaves, even more than Ti_8C_{12}, as a mixed-valence cluster. As for Ti_8C_{12}, an "intervalence transfer band" can be
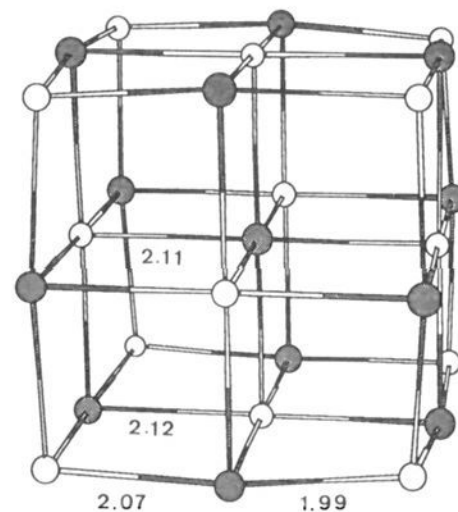
(39) Marksteiner, P.; Weinberger, P.; Neckel, A.; Zeller, R.; Dederichs, P. H. *Phys. Rev. B* **1986**, *33*, 812.

(40) The Mulliken point charge obtained for the peripheral carbon atoms in the neutral molecule is −1.44e. The charge of the central carbon is −2.84e. This very high value should be attributed at least in part to a problem of partitioning of the diffuse density, as previously encountered for the central oxygens in $[V_{10}O_{28}]^{6-}$.[41] One should notice, however, that the computed point charge of carbon in the lowest quintet states of Ti_8C_{12} is −0.67e.

(41) Kempf, J.-Y.; Rohmer, M.-M.; Poblet, J.-M.; Bo, C.; Bénard, M. *J. Am. Chem. Soc.* **1992**, *114*, 1136.

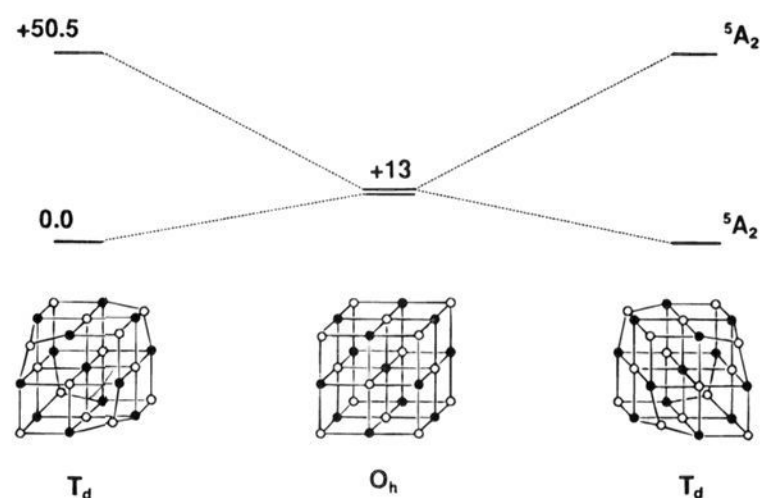**Figure 6.** Optimal structure (T_d symmetry) computed for the $Ti_{14}C_{13}$ crystallite in the $^5A_2$ state.

Figure 7. Potential energy diagram with twin minima (T_d, broken symmetry structures) and one maximum (O_h symmetry) computed for $Ti_{14}C_{13}$ (energies in kcal mol^{-1}).

characterized in the cluster with T_d symmetry by localizing the four metal electrons in the second set of four apical titanium atoms, connected to the carbon nearest neighbors by "short" $Ti-C$ distances of 1.992 Å. An excited quintet state is obtained at +50.5 kcal mol^{-1}. The doubly degenerate wave function with T_d symmetry obtained for the optimal O_h geometry (broken-symmetry solution) at +13 kcal mol^{-1} corresponds to the crossing between the two potential curves (Figure 7). It is well known that this crossing should be an avoided one, with a splitting depending upon the electron coupling integral J, whose value reflects the more or less delocalized character of the orbitals susceptible to accommodate the unpaired electron(s). The J factor was not estimated in the present work, but its order of magnitude is assumed to remain very small owing to the lack of interaction, either through-space or through-bond between the d_{z^2}-like orbitals susceptible to accommodate the unpaired electrons in either set of apical atoms. As an indication for the lack of interaction, the singlet−quintet energy splitting was computed to be no more than 6 cm^{-1}. The potential energy curve for the ground state of $Ti_{14}C_{13}$ is therefore expected to retain the shape of a double well.

VI. Summary and Conclusion

The goal of this paper is to investigate the electronic structure of the Ti_8C_{12} and $Ti_{14}C_{13}$ clusters, which are both expected to display exceptional stability. The attention is focused on the necessity to relocalize the d electrons on specific metal atoms in order to obtain an unbiased description of the electronic ground state. The requirement for a proper localization of metal electrons invalidates the aufbau principle as a criterion for predicting the electronic structure of metallocarbohedrenes. It is shown that the geometric structure most probable for Ti_8C_{12} is a tetracapped tetrahedron of metal atoms bridged by six C_2

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units, as first proposed by Dance.[6] Four d electrons are localized on the capping metal atoms and coupled into a singlet ground state with A_1 symmetry. CI expansions correlating the 20 metal electrons of the Ti_8C_{12} lead to an energy difference of 10.5 kcal mol^{-1} with respect to the $^5A_2$ state corresponding to the high-spin coupling of those four electrons. Six other local minima are characterized at the one-configuration SCF level on the potential hypersurface of Ti_8C_{12}. The SCF energies of those minima are scattered between +36 kcal mol^{-1} and +197 kcal mol^{-1} with respect to the SCF quintet state of the conformation with T_d symmetry. However, a proper localization of the 20 metal electrons by means of CI expansions consistently gathers the energies of the six secondary minima at $\sim$+160 kcal mol^{-1} with respect to the T_d form. The structure of pentagonal dodecahedron with T_h symmetry initially proposed to account for the special stability of Ti_8C_{12} corresponds to an energy *maximum* for the quintet electronic configuration correlating with the low energy $^5A_2$ state of the T_d form, and also for the nonet ^9A_g configuration that was found by Hay to be the ground state of the T_h form.[5]

In the $Ti_{14}C_{13}$ crystallite, 52 doubly occupied orbitals account for the titanium—carbon bonding. This bonding is formally best interpreted in terms of a covalent coupling between the 52 valence electrons of neutral carbon and the same number of d metal electrons. The four additional electrons are not involved in bonding and remain localized on four apical metal atoms, thus breaking into T_d the O_h symmetry first assumed for the crystallite. The energy difference between the high-spin ($^5A_2$) and the low-spin ($^1A^1$) couplings of those four electrons does not exceed 6 cm^{-1}, reflecting the lack of interaction between the d_{z^2}-like orbitals accommodating the unpaired electrons. It is therefore expected that the $Ti_{14}C_{13}$ crystallite behaves as a mixed-valence cluster, with a very small J factor. The potential energy curve is expected to retain the shape of a double well separated by a barrier of $\sim$13 kcal mol^{-1}.

Note Added in Proof. Since this work has been accepted for publication, the existence of two distinct metallic sites has been evidenced on the $V_8C_{12}^+$ ion by means of Fourier transform ion cyclotron resonance (Yeh, C. S.; Afzaal, S.; Lee, S. A.; Byun, Y. G.; Freiser, B. N. *J. Am. Chem. Soc.* **1994**, *116*, 8806). It could also be of interest to notice that the transformation of structure **2** into structure **1** or **3** schematized in Figure 3 of the present work had been considered from the academic viewpoint of group theory well before the characterization of met-cars (Cotton, F. A. *Chemical Applications of Group Theory*, 2nd ed.; Wiley-Interscience, New York, 1971; p 60, Exercises 3.16 and 3.17).

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