

# Quantum-chemical simulation of the interaction between the $\text{Ti}_8\text{C}_{12}$ metallocarbohedrene and the $\text{CHCl}_3$ molecule

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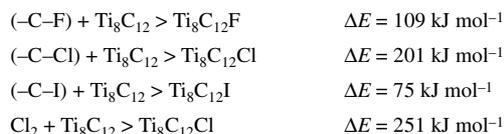
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The interactions of the  $\text{Ti}_8\text{C}_{12}$  metallocarbohedrene with halogen-containing addends are discussed on the basis of *ab initio* calculations of the  $\text{Ti}_8\text{C}_{12}(\text{CHCl}_3)$  adduct.

Pioneering studies of the reactivity of a new class of cage-like molecular nanostructures,<sup>4–6</sup>  $\text{M}_8\text{C}_{12}$  metallocarbohedrenes ( $\text{M} = d$ -metals), interacting with three types of addends (polar,  $\pi$ -bonding and halogen-containing molecules) were carried out.<sup>1–3</sup> We performed a quantum-chemical analysis of the interactions between  $\text{Ti}_8\text{C}_{12}$  and  $\pi$ -bonding molecules of ethylene and considered the formation mechanism of coordination bonding between the addend and the  $\text{Ti}_8\text{C}_{12}$  met-car taking the  $\text{Ti}_8\text{C}_{12} \times (\text{C}_2\text{H}_4)_4$  adduct as an example.<sup>7</sup>

As is known,<sup>8</sup>  $\text{Ti}_8\text{C}_{12}$  has an open electronic shell, which makes it a potentially active reactant in redox reactions. Of particular interest is the interaction of  $\text{Ti}_8\text{C}_{12}$  with halogen-containing addends. In this case, the following processes may take place: the reduction of a halogen (Hal), addend degradation and the formation of the stable adduct  $\text{Ti}_8\text{C}_{12}\text{-Hal}$ . Using the energies of chemical bonds,<sup>9</sup> the probabilities of the transformations  $\text{Hal-R} + \text{Ti}_8\text{C}_{12} > \text{Ti}_8\text{C}_{12}\text{-Hal} + \text{R}^0$  can be compared. Below are given some estimates [ $\Delta E \approx E(\text{Ti-Hal}) - E(\text{Hal-R})$ ] for the reactions



It can be seen that the formation of met-car adducts with chlorine-containing reactants is the most probable process.

The nature of such transformations can be described by the charge-fluctuation model.<sup>10</sup> The gist of the proposed model boils down to the following. Electronic density transfer from one reactant to another leads to a local deformation of the molecule and may bring about its destruction. In terms of the molecular orbital (MO) theory, this means that either antibonding MO become occupied or bonding MO get empty. As a result, the corresponding interatomic bonds weaken, and their fluctuation frequencies decrease to a certain 'critical' level ( $\omega \leq kT/\hbar$ ) and subsequent thermal dissociation.

To study the rearrangement of electronic states of the met-car when it interacts with halogen-containing reactants, we carried out *ab initio* calculations of the electronic energy structure (EES) of the  $\text{Ti}_8\text{C}_{12}(\text{CHCl}_3)$  complex, which is an adduct of  $\text{Ti}_8\text{C}_{12}$  with chloroform (Figure 1). The self-consistent nonempirical discrete variation (DV) method of electronic density functional was used in the computations.<sup>11</sup> Its details and the results of DV investigations of  $\text{Ti}_8\text{C}_{12}$  with  $T_h$  and  $T_d$  symmetry were published elsewhere.<sup>8</sup> The number of integration points was 30000. The  $\text{Ti}_8\text{C}_{12}(\text{CHCl}_3)$  complex possesses no space symmetry.

The model densities of states (MDOS) of  $\text{Ti}_8\text{C}_{12}(\text{CHCl}_3)$  and  $\text{CHCl}_3$  molecules are presented in Figure 2. Effective atomic charges ( $Q_{\text{eff}}$ ) and bond populations (BP) are listed in Table 1. When the adduct is formed, the states of chlorine atom [Cl(1)], through which a chloroform molecule is coordinated, undergo the greatest changes. These changes concern the bonding MO  $\psi_1$  with an energy of  $\sim(-8)$  eV, which is comprised of C  $2p$ - and Cl  $3p$ -AO, and the corresponding vacant antibonding MO  $\psi_2$  with an energy of  $\sim(+4)$  eV (Figure 2). It can be seen that the

$\psi_1$  MO has a large bonding energy and is not capable of participating in the stabilization of two-electron interactions with vacant  $\text{Ti}_8\text{C}_{12}$  MO. The four-electron interactions with occupied  $\text{Ti}_8\text{C}_{12}$  MO destabilise the complex (for more information about the effect of interorbital interaction types on the chemical stability of adducts see refs. 7 and 12). On the contrary, the energy of the antibonding  $\psi_2$  MO of the molecule decreases sharply when it interacts with  $\text{Ti}_8\text{C}_{12}$  (Figure 2), and this orbital in the complex becomes partially occupied. Consequently, stabilising interactions here are the so-called zero-electron interactions.

The data make it possible to consider the interactions of halogen-containing reactants with met-cars including those in condensed states. In the latter case, assume that the energy spectrum of the 'nanocrystalline carbide' is characterised by the Fermi energy ( $E_F$ ), and a chloroform molecule interacts with the 'active centre' of the nanocrystal surface according to Figure 1. When the molecular orbital  $\Psi = 2^{-1/2}[\psi_2 + \varphi(\text{Ti})]$  is formed (Figure 3), this interaction can be described by a linear three-atom fragment  $-\text{C-Cl(1)-Ti-}$  model. It follows from the computations that this MO is bonding relative to  $[\text{Cl(1)-Ti}]$  and antibonding relative to  $[\text{C-Cl(1)}]$  interactions. Further transformations of the  $\text{CHCl}_3$  molecule are determined by the relative position of  $E_F$  of the nanocrystal (HOMO of 'isolated' met-car) and the energy of the considered MO  $E(\Psi)$ . If  $E(\Psi) > E_F$ , the  $[\text{C-Cl(1)}]$  bonding energy experiences no considerable changes, and the stability of  $\text{CHCl}_3$  is retained. This situation is analogous to the interaction of  $\text{Ti}_8\text{C}_{12}$  with ethylene<sup>7</sup> when coordination bonding is formed between the addend and  $\text{Ti}_8\text{C}_{12}$  without dissociation of the former. When  $E_F > E(\Psi)$ ,  $\Psi$ -MO becomes occupied. As a result, the  $\text{CHCl}_3$  molecule dissociates due to its antibonding character [relative to the  $\text{C-Cl(1)}$  interaction]:  $\text{Ti}_8\text{C}_{12}(\text{CHCl}_3) > \text{Ti}_8\text{C}_{12}\text{Cl} + \text{CHCl}_2$ . In the case under consideration (for 'isolated' met-car), we observe a 'borderline' situation:  $E_F(\text{HOMO}) \sim E(\Psi)$ . Table 1 indicates that the BP  $[\text{C-Cl(1)}]$  here decreases considerably.

The qualitative criterion for dissociation of chemical bonds in the addend (or adsorbate molecule) occurring when the adduct (adsorption complex) is formed can be formulated on the basis of the obtained results in the following way. Dissociation will take place if the antibonding MO responsible for the chemical bonding in question stabilises as a result of interaction with the MO of nanoparticle atom (or energy state of the active centre of

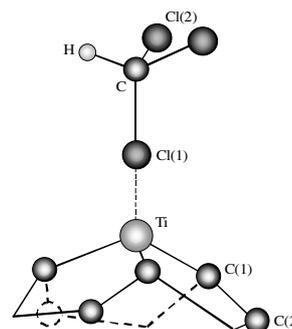
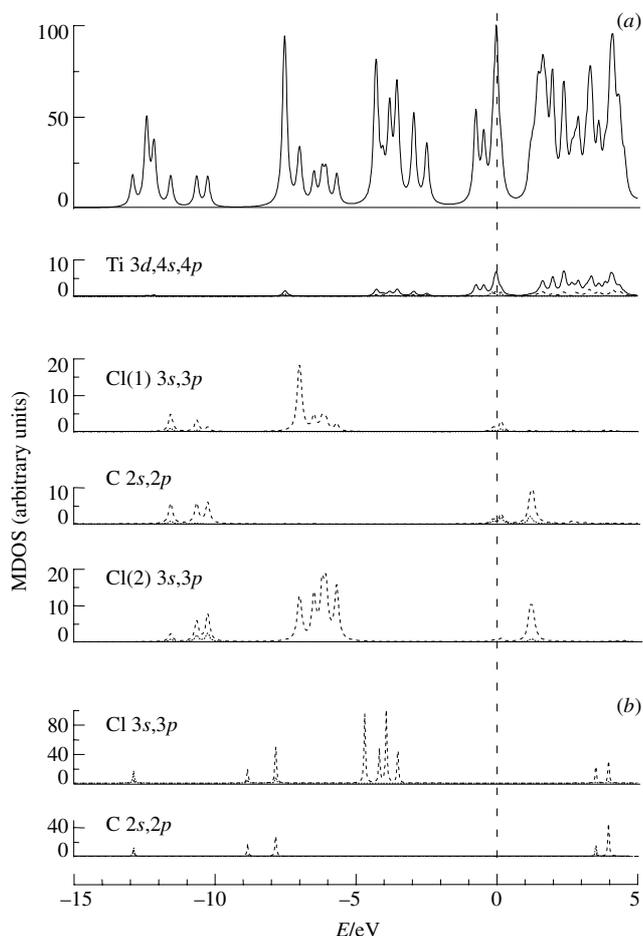


Figure 1 Coordination of a chloroform molecule to  $\text{Ti}_8\text{C}_{12}$ .

**Table 1** Calculation results of  $\text{Ti}_8\text{C}_{12}\text{Cl}$  and  $\text{Ti}_8\text{C}_{12}\text{Cl}_2$  complexes. Mulliken charges on atoms and FB of AO of chlorine atom in  $\text{Cl}_2$  molecule are given.

	$Q(\text{Ti})$	$Q[\text{C}(1)]^a$	$Q[\text{C}(2)]$	$Q[\text{Cl}(1)]$	$Q[\text{Cl}(2)]$	$Q(\text{C})$	$Q(\text{H})$	BP(Cl–C)/ $10^{-4}$ e		
								3p–2s	3p–2p	3s–2s
$\text{CHCl}_3$	—	—	—	–0.02	–0.02	–0.19	0.24	1491	2923	611
$\text{Ti}_8\text{C}_{12}(\text{CHCl}_3)$	1.02	–0.70	–0.72	0.04	–0.01	–0.18	0.00	815	1733	410

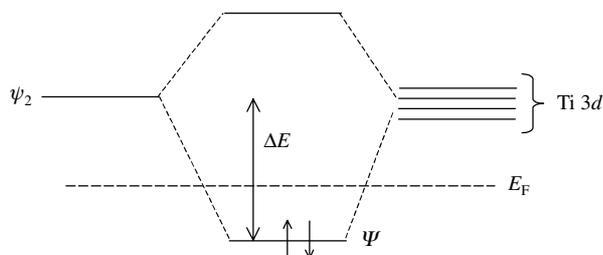
<sup>a</sup>C(1) and C(2) are nonequivalent C atoms in the  $T_h$   $\text{Ti}_8\text{C}_{12}$  structure.<sup>7</sup>



**Figure 2** Model densities of states (MDOS) of (a) the  $\text{Ti}_8\text{C}_{12}(\text{CHCl}_3)$  adduct and (b) the free molecule  $\text{CHCl}_3$ . Self-consistent DV calculations.

nanocrystalline substrate) in such a way that it becomes below the HOMO of the nanoparticle (below the Fermi level of the nanocrystal).

Let us consider the conditions when this criterion is met. In the above example, the fulfilment of this criterion is favoured by considerable values of the overlap integrals of  $\text{Ti}(3d,4p)$ - and  $\text{Cl}(1)(3p)$ -AO and similar energies of the antibonding orbital  $\psi_2$  of the molecule and vacant MO of  $\text{Ti}_8\text{C}_{12}$ . This ensures the stabilization energy  $\Delta E > [E(\psi_2) - E_F]$ . Therefore, the formation of a stable adduct with addend dissociation depends not only on



**Figure 3** Orbital interactions in the reaction of a halogen-containing addend with a titanium atom of  $\text{Ti}_8\text{C}_{12}$ . The formation of the antibonding MO  $\Psi$  and its location relative to the HOMO of the met-car ( $E_F$  of nanocrystalline 'titanium carbide') and the antibonding orbital  $\psi_2$  of the addend (chloroform molecule) are shown for the three-atom fragment  $-\text{C}-\text{Cl}(1)-\text{Ti}-$ .

the total stabilization energy  $\Delta E$ , but also on the  $[E(\psi_2) - E_F]$  value, i.e., the energy interval between the antibonding MO of the addend and the HOMO of a nanoparticle (the Fermi level of a nanocrystal). For halogen-containing addends, this condition is fulfilled fairly well.

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