

Studies of Met-Car Adducts: $\text{Ti}_8\text{C}_{12}^+(\text{M})_n$ ($\text{M} = \text{Halogens}, \pi\text{-Bonding Molecules}, \text{ and Polar Molecules}$)

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Received May 11, 1995[⊗]

Abstract: A new method of forming Met-Car–ligand complexes, $\text{Ti}_8\text{C}_{12}^+(\text{M})_n$ ($\text{M} = \text{halogens}, \pi\text{-bonding molecules}, \text{ and polar molecules}, n = 1\text{--}8$) is reported which involves the direct interaction of titanium with mixtures of methane and selected reactant gases. The results show that the formation of Ti_8C_{12} in the plasma is kinetically and thermodynamically favored over other reaction processes. Through an examination of Met-Car–ligand complexes, various reaction mechanisms of $\text{Ti}_8\text{C}_{12}^+$ are identified and characterized, namely oxidation, complexation, and ion–dipole interaction. Oxidation of $\text{Ti}_8\text{C}_{12}^+$ occurs when Met-Cars react with halogen-containing molecules through valence electron donation from $\text{Ti}_8\text{C}_{12}^+$ to the halogen atoms. When $\text{Ti}_8\text{C}_{12}^+$ interacts with π -bonding molecules, the findings are consistent with the formation of “surface complexes” comprised of the ligand binding across two of the metal atoms in the pentagonal ring of $\text{Ti}_8\text{C}_{12}^+$ through d– π interaction. In these cases, the cluster size distributions in the mass spectra of the reaction products exhibit truncation at $\text{Ti}_8\text{C}_{12}^+(\text{M})_4$. By contrast, ion–dipole interactions lead to the formation of $\text{Ti}_8\text{C}_{12}^+(\text{M})_{1\text{--}8}$ (M denoting polar molecules), which is consistent with previous findings showing that polar molecules bond to each metal site. The product distribution of $\text{Ti}_8\text{C}_{12}^+$ with butanol at various pressures provides new evidence which serves to resolve controversies in the literature regarding observed truncations and their implications concerning the geometric structure of $\text{Ti}_8\text{C}_{12}^+$; the findings are supportive of the originally proposed T_h symmetry. Furthermore, the further reaction of $\text{Ti}_8\text{C}_{12}^+(\text{I})$ with methanol, which gives the product distribution truncation at $\text{Ti}_8\text{C}_{12}^+(\text{I})(\text{CH}_3\text{OH})_7$, indicates that the titration method is a useful tool to probe the cluster structures in these systems.

Introduction

Metallocarbohedrenes, or Met-Cars, with the stoichiometry M_8C_{12} (M stands for early transition metals) were discovered in early 1992.¹ In the last 3 years, extensive studies have focused on the structure and properties of these novel cluster molecules. Theoretically, it has been shown that Met-Cars are stable species and may be useful building blocks for new materials.^{2–16} Considering the geometric structure of Met-Cars, a T_h symmetry was originally proposed by Guo and co-workers;¹ however, several other geometric structures for Met-Cars have also been proposed and many calculations favor a T_d symmetry.^{17–21} More recently, experimental studies have revealed

the existence of additional members of the Met-Car family including binary element Met-Cars,^{22–28} which show that they comprise a new form of carbide with cage-like structures. Some valuable information about the structures and energetics of these species has been obtained by employing metastable dissociation,^{29–30} photodissociation,^{31–33} and collision-induced dissociation.^{34–35} Also, recently Bowers and co-workers measured the mobilities of $\text{Ti}_8\text{C}_{12}^+$ and its fragments by using ion

[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1996.

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chromatography, and also concluded that Met-Cars most likely have a dodecahedral-type hollow cage-like structure.³⁶ However, unresolved anomalies have arisen from the results of studies of their chemistry with some results supporting the T_h while others seeming to support the T_d structure. Explaining these differences is one of the main focuses of the present paper.

As for the chemistry of Met-Cars, it has been found that $Ti_8C_{12}^+$ can sequentially associate with up to 8 water, ammonia, and CH_3OH polar molecules, and up to 4 nonpolar molecules such as C_6H_6 and C_2H_4 .³⁷ A reactivity change from $Ti_8C_{12}^+$ to $Ti_7NbC_{12}^+$ is observed upon reaction with acetone and methyl iodide.³⁸ Unlike $Ti_8C_{12}^+$, $Nb_8C_{12}^+$ and $V_8C_{12}^+$ can undergo "real chemical reactions" with polar molecules,^{38,39} involving the breaking and forming of chemical bonds in addition to ligand association. These various studies have raised some questions: (1) Why does $Ti_8C_{12}^+$ have different coordination numbers when reacting with differing types of molecules; (2) which one of the proposed structures of $Ti_8C_{12}^+$, T_d or T_h symmetry, can be supported by experimental findings; and (3) why can $Ti_8C_{12}^+$ only taken one I atom from MeI? In order to answer these questions and obtain a clearer picture about the reactivities of $Ti_8C_{12}^+$ and their structural complications, recent work was undertaken in our laboratory on the formation of Met-Car adducts, $Ti_8C_{12}^+(M)_n$ (M = halogens, π -bonding molecules, and polar molecules); the new findings are reported herein.

Two methods are used to produce Met-Car adducts: one is through the interaction of $Ti_8C_{12}^+$ with neutral reactants, and the other is through the laser-induced plasma reaction of titanium with mixtures of methane and reactant gases. By examining these Met-Car adducts, it is found that Met-Cars can display three classes of reactivities, namely oxidation, complexation, and ion-dipole interaction, which lead to different reaction products. One particularly important result is that the new findings validate the titration method for interrogating these classes of cluster systems. Then, through an analysis of the maximum coordination number for these reactions, additional evidence for the geometric structures of Met-Cars is obtained.

Experimental Section

A triple-quadrupole mass spectrometer coupled with a laser vaporization source is used in the present studies; details of the experimental setup are given elsewhere.³⁴ Briefly, the second-harmonic output of a Nd:YAG laser is used to ablate the surface of a rotating titanium rod. Then titanium is vaporized and, through plasma reactions with methane or a mixture of methane and reactant gases which are carried in helium buffer gas, metal-carbon clusters are produced. After exiting the source and passing through the skimmer, the formed cation clusters are focused and steered by the first group of three electrical ion lenses, and horizontal and vertical deflector plates, into the first quadrupole mass filter. Using this filter, a cluster of the desired size can be mass-selected. Thereafter, the selected clusters are refocused and deflected by a second group of ion lenses and deflectors, and then injected into a second quadrupole mass filter. This one, which is operated in the RF-only mode, serves as either a reaction cell or a collision cell. The reactant or collision gas is introduced into this cell where its pressure is monitored by a capacitance manometer (MKS). After reactions or collisions of these size-selected clusters with the reactant or collision gas, the products drift out of the cell. Thereafter, they enter the third quadrupole mass filter, in which the products are analyzed, and are then detected by a channeltron electron multiplier coupled with the mass filter. When the first quadrupole mass filter is operated in the RF-only mode, the total cluster distribution from the plasma reactions is obtained.

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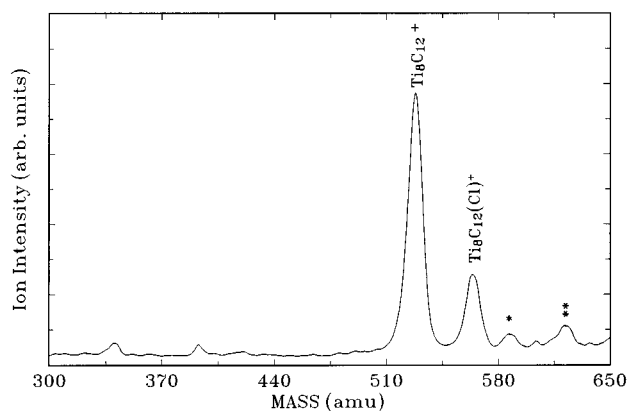


Figure 1. Mass spectrum of $Ti_8C_{12}^+$ interacting with $CHCl_3$. The peaks marked by one and two asterisks are due to residual acetone impurity from a prior measurement.

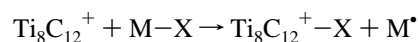
The cluster ion distributions in the present experiments are identical to those reported previously,¹ i.e., $Ti_8C_{12}^+$ is the dominant species and corresponds to 90% of the total ion intensity. The isotope pattern of $Ti_8C_{12}^+$ is clearly observed at high resolution. However, for most of the work reported herein, the resolution of the first mass filter is intentionally decreased in order to obtain a high concentration of $Ti_8C_{12}^+$ for studying its reactions in the second quadrupole mass filter. The methane concentration in the helium carrier gas is maintained at about 15%. The typical concentration of reactant gases is about 1% in the mixture of the reactant, methane, with helium, or 0.1 to 3.0 mTorr of pure reactant gas in the reaction cell. The entrance voltage of the reaction cell is normally set between 0 and +1 V with respect to the region of Met-Car production (ground potential). This selection of potentials ensures that the reactions occur at or near thermal energies.

Results

1. Formation of Met-Car Adducts by Thermal Reactions.

The method to produce Met-Car adducts has been discussed in previous publications.^{37,38} It had been found that in addition to sequentially associating up to 8 polar molecules (e.g. H_2O , CH_3OH , and NH_3), and up to 4 nonpolar molecules (C_6H_6 and ethylene), $Ti_8C_{12}^+$ can abstract one iodine atom from methyl iodide. In the present work, a number of other gases are used to react with $Ti_8C_{12}^+$. These reactant gases can be divided into three categories: (1) halogen-containing molecules, such as Cl_2 , $CHCl_3$, C_6H_5Cl , and CH_2F_2 ; (2) π -bonding molecules, such as CH_3CN , pyridine, and acetone; and (3) a moderate size polar molecule, 2-butanol. Although the experimental method used in this work, triple quadrupole mass spectrometry, is different from the ion drift tube technique used in the previous work, similar product distributions for certain reactions are obtained. This implies that the nonthermal energies in triple quadrupole mass spectrometry do not have significant influence on the reaction mechanisms and product distributions. These reactants were chosen for specific reasons as discussed below.

The common reaction channel for $Ti_8C_{12}^+$ reacting with halogen-containing molecules is one halogen atom abstraction, which can be represented as follows:



Here, $M-X$ denotes a halogen-containing molecule. Two minor reaction channels that we observe include the sequential addition of MX onto $Ti_8C_{12}^+$ for C_6H_5Cl and CH_2F_2 and sequential attachment of a second X onto $Ti_8C_{12}^+-X$ only for the case of Cl_2 gas. A typical product mass spectrum of these reactions is displayed in Figure 1 for the reaction of $Ti_8C_{12}^+$ with $CHCl_3$.

As mentioned in previous papers,^{37,38} the reaction of $Ti_8C_{12}^+$ with π -bonding molecules is mainly through an association mechanism. No bond breaking is observed in the present work

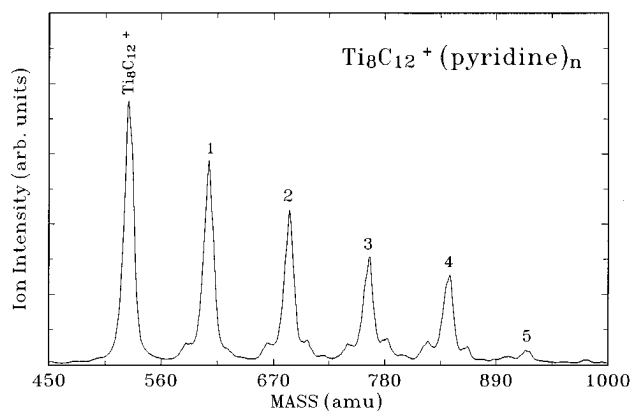


Figure 2. The mass spectrum of $\text{Ti}_8\text{C}_{12}^+$ with pyridine. The numerals indicate the number of pyridines associating onto $\text{Ti}_8\text{C}_{12}^+$. Note that the distribution truncates at $n = 4$.

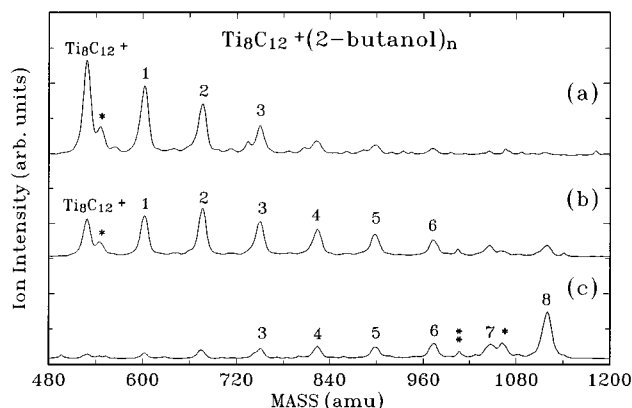


Figure 3. The mass spectrum of $\text{Ti}_8\text{C}_{12}^+$ with 2-butanol at different pressures: (a) 0.65 mTorr, (b) 0.8 mTorr, (c) 1.20 mTorr. The numerals indicate the number of butanols associating onto $\text{Ti}_8\text{C}_{12}^+$. Note that a smooth transition in the number of 2-butanol binding onto $\text{Ti}_8\text{C}_{12}^+$ occurs with the increase of pressure of 2-butanol; the distribution truncates at $n = 8$. The peaks marked by one and two asterisks are due to water and methanol impurities.

either. In the reaction of $\text{Ti}_8\text{C}_{12}^+$ with pyridine, it is found that only one and two pyridine molecules attach to $\text{Ti}_8\text{C}_{12}^+$ when the pressure of pyridine is lower than 0.5 mTorr. Increasing the pressure of pyridine leads to more pyridine additions, whereupon a product distribution truncation at $\text{Ti}_8\text{C}_{12}^+(\text{pyridine})_4$ eventually can be observed. The mass spectrum of reaction products of $\text{Ti}_8\text{C}_{12}^+$ with 0.7 mTorr of pyridine is displayed in Figure 2. Very small peaks attributable to $\text{Ti}_8\text{C}_{12}^+(\text{pyridine})_{5,6}$ can also be seen in this figure. But, further increasing the pressure of the reactant gas up to 2.0 mTorr does not change the number or relative intensities of these association products. The reactions of $\text{Ti}_8\text{C}_{12}^+$ with both acetone and CH_3CN yield similar distributions, which result in a product distribution truncation at $\text{Ti}_8\text{C}_{12}^+(\text{acetone})_4$ and $\text{Ti}_8\text{C}_{12}^+(\text{CH}_3\text{CN})_4$, respectively. Similar to the pyridine results shown in Figure 2, small peaks corresponding to $\text{Ti}_8\text{C}_{12}^+(\text{acetone})_{5,6}$ and $\text{Ti}_8\text{C}_{12}^+(\text{CH}_3\text{CN})_{5,6}$ are usually observable.

In the case of polar molecules, a rather different truncation is invariably obtained. This is observable in the mass spectrum of the product distribution of $\text{Ti}_8\text{C}_{12}^+$ with 2-butanol at different pressures; see Figure 3. A cluster distribution truncation at $\text{Ti}_8\text{C}_{12}^+(\text{2-butanol})_8$ is clearly evident. As evidenced by the results shown in Figure 3a–c, careful studies over a range of pressures failed to reveal any evidence of a truncation or other break in the smooth distribution representative of ligand attachments.

2. Formation of Met-Car Adducts by Plasma Reactions.

In this phase of the work, four reactant gases (benzene, acetone,

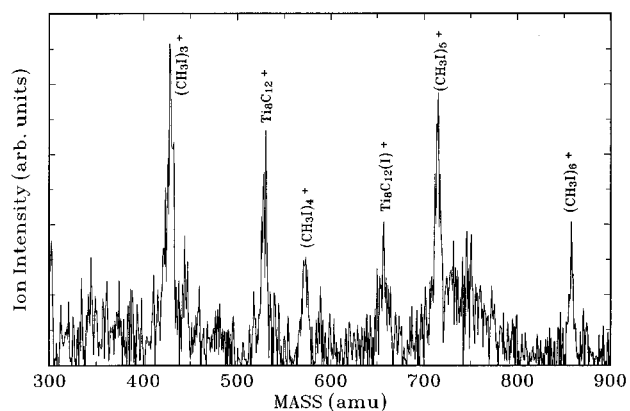


Figure 4. Mass spectrum of the plasma reaction of titanium and the mixture of methane/methyl iodide/helium.

methyl iodide, and methanol) are used individually to make the desired mixtures with methane. In the absence of methane, it is found that at a concentration of about 1% in helium gas, all four reactants react individually with vaporized titanium to produce various products. Loss of some hydrogen atoms occurs in the case of acetone, benzene, and methanol. However, when methane at a concentration of 15% is mixed into these gases under essentially the same laser-plasma conditions, the product distribution is completely altered. The mass spectrum of plasma reaction products of Ti with a mixture of methane, methyl iodide, and helium is exhibited in Figure 4. In this spectrum, several peaks with enhanced intensities are observed and mass-assigned as $\text{Ti}_8\text{C}_{12}^+$, $\text{Ti}_8\text{C}_{12}^+(\text{I})_1$, and $(\text{MeI})_{3-5}^+$.

In order to first prove that the peak with a mass of 655 amu is $\text{Ti}_8\text{C}_{12}^+(\text{I})$, this species is mass selected and probed by using collision-induced dissociation (CID). CID experiments were carried out under multiple-collision conditions with pressures of 0.7 to 0.8 mTorr. The sole CID product of this species is $\text{Ti}_8\text{C}_{12}^+$, which establishes that Met-Car adducts can be produced directly in the plasma reactor. The plasma reactions of $\text{Ti}_8\text{C}_{12}^+$ with acetone, methanol, and benzene give the products in which $\text{Ti}_8\text{C}_{12}^+(\text{M})_{1,2}$ and $(\text{M})_n^+$ (M designating these three reactant molecules) are the dominant species in the distribution.

Titration reactions have been used successfully to probe cluster structures.⁴⁰ The key in applying titration reactions to determine the structure of Met-Cars is assuming that these reactions occur at metal centers and that one metal can associate with only one reactant molecule. In order to support this assumption, $\text{Ti}_8\text{C}_{12}^+(\text{I})$ formed from the plasma reaction of titanium with a mixture of methane and methyl iodide was mass selected and its reaction with methanol was studied. Although iodide and methanol have different bonding properties toward $\text{Ti}_8\text{C}_{12}^+$, a maximum of seven methanol attachments to $\text{Ti}_8\text{C}_{12}^+(\text{I})$ are expected according to our assumption. The mass spectrum of the reaction of $\text{Ti}_8\text{C}_{12}^+(\text{I})$ with methanol is displayed in Figure 5. From this spectrum, it is found that one to seven methanols attach to $\text{Ti}_8\text{C}_{12}^+(\text{I})$, and a cluster distribution termination at $\text{Ti}_8\text{C}_{12}^+(\text{I})(\text{methanol})_7$ is observed. This is to be contrasted with the previously observed distributions³⁷ obtained under similar conditions for the non-halogen-containing Met-Car, leading to the truncation at $\text{Ti}_8\text{C}_{12}^+(\text{methanol})_8$. Taken together, these results show that eight metal atoms in $\text{Ti}_8\text{C}_{12}^+$ are reactive centers and one titanium atom can associate with only one reactant molecule.

Discussion

First, we consider the formation of the Met-Car adducts produced through plasma reactions of titanium with the mixtures

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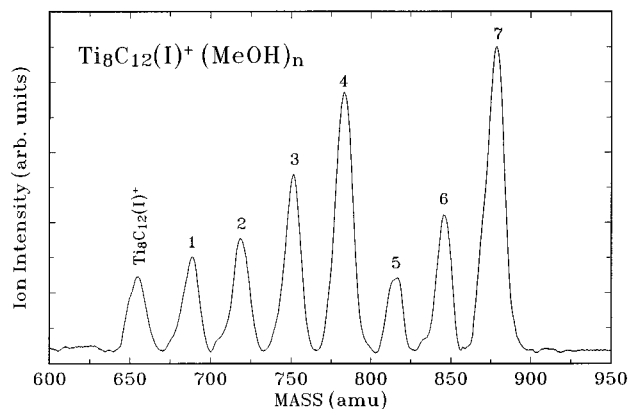


Figure 5. Mass spectrum of $\text{Ti}_8\text{C}_{12}^+(\text{I})$ with methanol. The numerals indicate the number of methanols associating onto $\text{Ti}_8\text{C}_{12}^+$. Note that the association reactions terminate at the seventh step.

of methane, reactant gas, and helium. As previously mentioned, without methane, titanium can individually react with all four organic molecules under similar experimental conditions, leading to various non-Met-Car-containing products. With methane, there are two competitive reactions: titanium reacting with methane in the plasma to produce $\text{Ti}_8\text{C}_{12}^+$, which can further react with neutral reactants leading to the formation of $\text{Ti}_8\text{C}_{12}^+$ adducts, and titanium undergoing individual reactions with these reactants leading to partially dehydrogenated species. From the reaction product distribution, it is clearly seen that under the present experimental conditions, the formation of $\text{Ti}_8\text{C}_{12}^+$ is energetically and/or kinetically favored over the other reaction products which again shows that $\text{Ti}_8\text{C}_{12}^+$ has considerable stability. The formation of $\text{Ti}_8\text{C}_{12}^+$ adducts could occur in the supersonic expansion; in this sense, the formation mechanism of $\text{Ti}_8\text{C}_{12}^+$ adducts may be similar for both reaction processes.

The abstraction of a halogen atom from halogen-containing molecules is affected by the high electron affinities of halogen atoms. When $\text{Ti}_8\text{C}_{12}^+$ reacts with halogen-containing molecules, electrons can be donated from the valence orbital of $\text{Ti}_8\text{C}_{12}^+$ to the halogen atoms. The bonding between $\text{Ti}_8\text{C}_{12}^+$ and halogen atoms may have substantial ionic and covalent character, such as bonding in the ground state of CrCl^+ .⁴¹ Theoretical studies¹¹ found that the HOMO of $\text{Ti}_8\text{C}_{12}^+$ is a triplet state involving the $1e_u$ orbital. Therefore, only one electron is left in the HOMO for $\text{Ti}_8\text{C}_{12}^+$ and this electron may be easily transferred to the valence p orbital of the halogen atom, leading to the formation of an ionic compound. These considerations explain observations that the dominant reaction channel for $\text{Ti}_8\text{C}_{12}^+$ reacting with halogen-containing molecules is a one halogen atom abstraction.

It should also be noted that the referred to halogen abstraction reaction is energetically favored. The bond strengths of Ti–F, Ti–Cl, and Ti–I are 136, 118, and 74 kcal/mol, respectively. They are larger than the bond strengths of C–F (about 110 kcal/mol), C–Cl (about 70 kcal/mol), and C–I (about 56 kcal/mol).⁴² The strength of the Cl–Cl bond is only 58 kcal/mol. Thus, multi-chlorine abstraction products are expected when $\text{Ti}_8\text{C}_{12}^+$ reacts with the dichlorine molecule because the formation of two Ti–Cl bonds will release enough energy to promote the electron in the sub-HOMO of $\text{Ti}_8\text{C}_{12}^+$ to be involved in interactions with halogen atoms. In other cases, the energy released from the formation of Ti–X bonds will not be enough to promote electrons from the sub-HOMO of $\text{Ti}_8\text{C}_{12}^+$, which is a $2t_u$ orbital having six electrons, to enable interaction with the

halogen atoms. Since there are a total of 8 electrons in the HOMO and sub-HOMO orbitals of neutral Met-Cars, it is expected that its oxidation states may be varied from 0 to +8. We look forward to an examination of this conclusion from future electrochemical studies of Met-Cars.

In the present work, it is observed that the product distribution truncates at $n = 4$ for $\text{Ti}_8\text{C}_{12}^+(\text{acetone, pyridine, or CH}_3\text{CN})_n$; very small peaks of $\text{Ti}_8\text{C}_{12}^+(\text{acetone, pyridine, or CH}_3\text{CN})_{5,6}$ are also seen. These findings are consistent with previous studies³⁷ showing that a maximum of four ethylene and benzene molecules can associate onto $\text{Ti}_8\text{C}_{12}^+$. Two facts are of particular note: one is that acetone, CH_3CN , and pyridine are not only π -bonding molecules but also polar molecules; the other is that a cluster distribution truncation at $n = 4$ is observed for these three reactions. Therefore, it is logically suggested that π -bonding molecules associate to $\text{Ti}_8\text{C}_{12}^+$ differently than do non- π -bonding molecules. The above experimental results can be explained in terms of the cluster distribution truncation at $n = 4$, which is attributed to the special bonding character of π -bonding molecules discussed below.

Based on the numerous results on the uptake of molecules by $\text{Ti}_8\text{C}_{12}^+$, one consistent picture is emerging. In the case of polar molecules, at sufficiently high reactant concentrations eight are accommodated, even in the case of relatively sizable ones such as 2-butanol. For π -bonding ligands of various sizes, truncation occurs at $n = 4$, and for π -bonding molecules with appreciable dipole moments, a distinct truncation at $n = 4$, but with a minor distribution extending to somewhat higher degrees of attachment at high reactant pressures.

Although it is still not certain how $\text{Ti}_8\text{C}_{12}^+$ associates with four π -bonding molecules, it is suggested that this is related to the specific electronic and geometric structure of $\text{Ti}_8\text{C}_{12}^+$, a dodecahedron with twelve pentagonal rings. Based on this structure, one pentagonal ring has two titanium atoms and three carbon atoms, in which two carbons form a double bond. Each titanium atom has four valence electrons, in which three of them are used to form σ -bonds with three C_2 units, and one of them remains. Theoretical studies indicate titanium atoms in $\text{Ti}_8\text{C}_{12}^+$ have some net positive charge and their empty d-orbitals can act as electron acceptors. Therefore, when π -bonding molecules approach the pentagonal surface through d- π interaction, the double or triple bonds can lie atop two titanium atoms in the ring, and form complexes analogous to the molecule–surface complexes, or organometallic clusters.⁴³ There are eight Ti atoms in Ti_8C_{12} which can be grouped into four, two-metal-center bonding units. Accordingly, a maximum of four π -bonding molecules could be accepted, leading to a truncation at $\text{Ti}_8\text{C}_{12}^+(\pi\text{-bonding molecules})_4$, as observed for the reaction product distributions. The proposed structure for $\text{Ti}_8\text{C}_{12}^+(\text{C}_2\text{H}_4)_4$ is displayed in Figure 6. Ab initio calculations on $\text{Ti}_8\text{C}_{12}^+(\pi\text{-bonding molecules})_{1-4}$ are in progress, and preliminary results show that, for example, the binding energy of HCN lying parallel to the pentagonal ring surface is quite high.

Further minor attachments of acetone and CH_3CN leading to small peaks of five and six ligations are evidently due to the fact that these two molecules have relatively large dipole moments, and hence there is some competition of possible dipolar interactions with the more favored π -bonding arrangements. This argument also accounts for the further addition of water molecules onto the $\text{Ti}_8\text{C}_{12}^+(\text{benzene})_4$ complex reported earlier.³⁷

An alternative explanation which has been proposed³⁹ to account for the reaction products of Met-Cars with π -bonding molecules or polar molecules suggests the attachment to be

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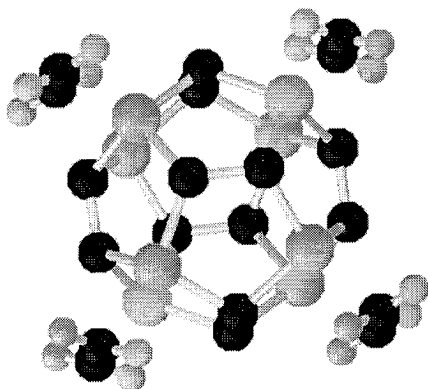


Figure 6. Model showing the bridging of four π -bonding molecules (C_2H_4) across two metal atoms of each pentagonal ring.

dependent mainly on the geometric structures of Met-Cars. It is theoretically predicted that Met-Cars with T_d symmetry are more stable than those with T_h symmetry.¹⁹ On the basis of these considerations, if species with T_d symmetry are favored, they would be expected to have two types of metal atoms. One type is calculated to have four metal atoms located at an outer position, having a +3 oxidation state, while the other four metal atoms are predicted to have an inner position with 0 oxidation state. Therefore, it is expected that these two sets of titanium atoms should have different reactivities, and it has been suggested³⁹ that this might cause the product distribution truncation at 4 when $Ti_8C_{12}^+$ reacts with π -bonding molecules. Based on this model, a prominent cluster distribution magic number or truncation at $Ti_8C_{12}^+(\text{polar molecules})_4$ should also be observed, but none has ever been seen. Rather, a smooth transition in the number of polar molecules accommodated followed by a truncation at $Ti_8C_{12}^+(\text{polar molecules})_8$ is observed in all experiments we have performed. The possibility that the ligand binding induces some structural transformation from T_d to T_h is ruled out based on the following considerations: (1) ab initio calculations²¹ indicate that this transformation needs more than 230 kcal/mol of energy; (2) CID of $Ti_8C_{12}^+(\text{methanol})$ shows that the bonding strength of $Ti_8C_{12}^+-CH_3OH$ is smaller than 1 eV, although accurate measurements of the bonding strengths of these adducts still have not been achieved. Therefore, the above discrepancy raises two questions: One is that the cluster distribution truncations at $Ti_8C_{12}^+(\text{polar molecules})_8$ are due to $Ti_8C_{12}^+$ which has T_h symmetry, or the reactant molecules display no difference that can be observed when they react with two different types of metal atoms (assuming that $Ti_8C_{12}^+$ has T_d symmetry). Another question is whether titration of Met-Cars is a suitable tool to probe their geometric structure, because no proof has been given that each metal atom in Met-Cars can accommodate only one neutral reactant molecule.

In order to clarify these arguments, we used 2-butanol as a reactant to react with $Ti_8C_{12}^+$; the resulting mass spectrum of the reaction products is shown in Figure 3. Referring to the figure, no obvious truncation at $Ti_8C_{12}^+(2\text{-butanol})_4$ is observed for any pressure of 2-butanol employed in these studies. According to previous studies,³⁷ this reaction would also be expected to take place through ion-dipole interactions. The interacting centers should be on the oxygen of 2-butanol and the titanium atoms of $Ti_8C_{12}^+$. The molecule 2-butanol was chosen for this study since it is large in comparison with other polar reactants used in previous studies.³⁷ Hence, its size should

give rise to some reduction in the bonding if steric hindrance plays some role in the resulting distributions. If there are two different types of titanium atoms in accord with the model of T_d symmetry, some evidence of a truncation at $Ti_8C_{12}^+(2\text{-butanol})_4$ should be seen, and the use of this molecule should enhance its observability. Yet no such evidence is found, and clearly a truncation only at $n = 8$ is seen from the data. Hence, the present experimental results, in addition to the mobility measurements of Met-Cars by Bowers and co-workers,³⁶ provide strong support for $Ti_8C_{12}^+$ having T_h symmetry as originally proposed.¹

The studies reported herein for the titration of the iodine-containing Met-Car $Ti_8C_{12}I^+$ provided further support for the usefulness of this method of gaining insights into structure. Further consideration of these results is also warranted. According to the T_h model, the presence of the iodine bound to one Ti will influence binding to three other metal atoms located in the three rings of which the Ti-I state is a member. It is likely that the three neighboring titanium atoms are different from the other four. This is expected to give rise to two different ligand binding distributions, a fact which is readily seen from the data given in Figure 5, where a higher intensity of $Ti_8C_{12}^+(I\text{-methanol})_4$ is observed. Hence, our data are in full agreement with the expectations for the T_h symmetry structure.

Conclusions

$Ti_8C_{12}^+$ adducts can be produced either by $Ti_8C_{12}^+$ cations reacting with reactant gases at thermal energies or by the plasma reaction of titanium with a mixture of methane and reactant gases. A general examination of our results of studies of $Ti_8C_{12}^+$ adducts shows that $Ti_8C_{12}^+$ can undergo three classes of reactions: abstraction of halogen atom(s) from halogen-containing molecules, association of π -bonding molecules with a cluster distribution truncation at $Ti_8C_{12}^+(\pi\text{-bonding molecules})_4$, and attachment of polar molecules with a cluster distribution termination at $Ti_8C_{12}^+(\text{polar molecules})_8$. Through an examination of the formation of these $Ti_8C_{12}^+$ adducts, it is found that $Ti_8C_{12}^+$ displays three different classes of reactivities, namely oxidation, complexation, and ion-dipole association. Oxidation of $Ti_8C_{12}^+$ occurs when $Ti_8C_{12}^+$ reacts with halogen-containing molecules. The high electron affinity of halogen atoms and the magnitude of titanium-halogen bond strength leads to electron transfer from $Ti_8C_{12}^+$ to the halogen atoms. Due to one electron in the HOMO of $Ti_8C_{12}^+$, one halogen abstraction product by $Ti_8C_{12}^+$ is the dominant species in all reactions of $Ti_8C_{12}^+$ with halogen-containing molecules. The complexation of $Ti_8C_{12}^+$ occurs when $Ti_8C_{12}^+$ reacts with π -bonding molecules. The π -bonds are believed to lie atop the two titanium atoms in one pentagonal surface, through d- π interaction, to form surface complexes. There are eight titanium atoms grouped into four non-neighboring pentagonal rings, and a cluster distribution truncation at $Ti_8C_{12}^+(\pi\text{-bonding molecule})_4$ is expected as observed in the mass spectra. The reaction product distribution of $Ti_8C_{12}^+$ with 2-butanol, which truncates at $Ti_8C_{12}^+(2\text{-butanol})_8$, gives more evidence that Ti_8C_{12} has T_h symmetry.

Acknowledgment. Financial support by the Air Force Office of Scientific Research, Grant No. F49620-94-1-0162, is gratefully acknowledged.