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Binary Metal Metallocarbohedrenes of Titanium and Group IIIA, VA, and VIA Metals

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Abstract: Binary metal metallocarbohedrenes of titanium and the metals yttrium, niobium, molybdenum, tantalum, and tungsten have been produced by the direct laser vaporization of mixtures of titanium carbide with these metals. Interestingly, as individuals metals, yttrium, tantalum, and tungsten have not displayed a tendency for forming the metallocarbohedrene (Met-Car) structure. Substitution of titanium atoms by these non-group IVA metals in the titanium Met-Car, Ti_8C_{12}, is not as extensive as that achieved with the group IVA metal zirconium under similar conditions. Recent theoretical predictions based upon electronic structure and nuclear charge[8,9] are considered in interpreting these results.

Introduction

Metallocarbohedrenes (Met-Cars) were originally discovered in 1992 by Guo et al.[1] while studying the reactions of laser-vaporized transition metals with gaseous hydrocarbons. The smallest members of the Met-Car class have the formula M_8C_{12} and a proposed pentagonal dodecahedron structure with T_h symmetry. Following the initial report on the existence of $Ti_8C_{12}^+$, subsequent investigations resulted in the production of the Zr, Hf, V, Cr, Fe, and Mo analogues.[2,3] Further studies by Wei et al.[4,5] have focused on the general formation mechanism of these species and yielded evidence for extended multicage structures in the zirconium system.

In all of these studies following the initial discovery, the Met-Car clusters were produced with a laser-induced plasma reactor[6] and studied via time-of-flight mass spectrometry. Typically, the transition metal of interest is vaporized into a hydrocarbon/buffer gas mixture, where reaction occurs; the products are subsequently expanded into vacuum. Thereafter, either Met-Car ions are extracted from the skimmed beam by pulsing voltages on the time-of-flight grids or ionization of neutral Met-Cars is accomplished with a second laser and the resulting ions are accelerated by constant voltages applied to the grids.

More recently, we reported the production of the metallocarbohedrenes of titanium and zirconium by the direct laser vaporization of the carbides of these metals.[7] These technique simplifies the production of Met-Cars by eliminating the carrier gas, supersonic expansion, and molecular beam conditions required by the laser-induced plasma reaction method. Futhermore, studying the production of metallocarbohedrenes by the laser vaporization of solid carbide targets sheds light on the relationship between the Met-Cars, with their 1:1.5 metal to carbon stoichiometric signature, and the recently reported stoichiometric cubic systems of titanium/carbon, vanadium/carbon, and niobium/carbon.[8,9] Also, this technique facilitates the production of mixed metal metallocarbohedrenes. We have shown that the laser vaporization of mixtures of metal and carbide powders produces binary metal metallocarbohedrenes,[10] in particular Met-Cars of the group IVA transition metals, $Ti_xZr_yC_{12}$ ($x + y = 8$) and $Ti_xHf_yC_{12}$ ($x + y = 8$). Here we report the production of binary metal Met-Cars of titanium in combination with the group IIIA, VA, and VIA metal yttrium, niobium, tantalum, molybdenum, and tungsten. Interestingly, only two of these metals have been observed to display Met-Car character. Molybdenum exhibits the "pure" Met-Car character,[3] while recent evidence indicates that the niobium/carbon system yields both the cubic and Met-Car structures.[9]

Experimental Section

Experiments were performed with a reflectron-equipped time-of-flight (TOF) mass spectrometer. As noted earlier, laser-induced plasma reactors coupled with TOF mass spectrometers have been used extensively in the production and study of metallocarbohedrenes. Such a method, however, requires a carrier gas, supersonic expansion, molecular beam conditions, and precise control over a complex timing scheme. The present experimental technique eliminates the carrier gas, supersonic expansion, and molecular beam conditions and reduces the complexity of the timing scheme by only requiring control over the delay between the vaporization and ion extraction events.

Samples of pure TiC (2.5–4 μm, 99%, Johnson–Matthey) and mixtures of TiC with the metals Y (200 μm, 99.9%), Nb (−325 mesh, 99.8%), Mo (−250 mesh, 99.9%), Ta (−325 mesh, 99.9%, and W (0.5 μm, 99.9%) were loosely packed into a boron nitride sample holder placed 4 cm below the center of the TOF extraction region. Vaporization of the sample of interest was accomplished with the partially focused (~1 mm spot size) second harmonic output (532 nm) of a Nd:YAG (Spectra Physics DCR-2) laser operated at 7 mJ/pulse. The vaporization laser was directed perpendicular to the mass spectrometer axis and continually rastered across the sample surface. Mass analysis of the ions formed above the sample following vaporization was accomplished by applying high-voltage pulses to the extraction (+2900 V DC) and acceleration (+2175 V DC) grids of the Wiley/McLaren design[11] TOF mass spectrometer. These pulses were generated by a fast, high-voltage transistor switch (Behlke

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HTS-81) that provided both short rise time and very stable output pulses. Following extraction within the TOF lens, the ions drift through a 2-m-long field-free region and are subsequently focused with a reflectron. Use of the reflectron in a focusing mode is necessary to compensate for the broad ion energy distribution resulting from the simultaneous acceleration of all the ions initially present in the extraction region. The ion signal was collected with a chevron multichannel plate (Galileo), averaged over 1000 laser shots, and stored by a 175-MHz digital storage oscilloscope (Lecroy 9400 A). Control of the time delay between the firing of the vaporization laser and the pulsing of the TOF voltages was accomplished with a home-built delay generator.

Results and Discussion

Figure 1a shows the high-mass range of a mass spectrum of $Ti_xC_y^+$ clusters obtained by vaporizing a pure titanium carbide target. Figure 1b-f shows, respectively, the spectra obtained from the vaporization of five separate mixtures of yttrium, niobium, molybdenum, tantalum, and tungsten with titanium carbide. In the mass range shown, the dominant peak in each spectrum is $Ti_8C_{12}^+$. Vaporization of a 30:1 molar mixture of titanium carbide and yttrium yields the spectrum shown in Figure 1b. Sustitution of one titanium atom by a yttrium, corresponding to $Ti_7Y_1C_{12}^+$, is evident. There is also peak at mass 610 amu with a substantially poorer signal to noise ratio, which suggests the doubly substituted species, $Ti_6Y_2C_{12}^+$. The group VA elements Nb and Ta form binary metal Met-Car species upon vaporization of 1:1 and 2:1 molar mixtures of titanium carbide with these metals. The singly and doubly substituted $Ti_7Nb_1C_{12}^+$ and $Ti_6Nb_2C_{12}^+$ species are observed in Figure 1c. Figure 1e shows the existence of the binary metal cluster $Ti_7Ta_1C_{12}^+$. Vaporization of 4:1 and 15:1 molar mixtures of titanium carbide with molybdenum and tungsten, respectively, yields the species $Ti_7Mo_1C_{12}^+$ and $Ti_7W_1C_{12}^+$, as seen in Figure 1d,f.

As reported recently, mixtures of titanium carbide and the group IVA metal zirconium yield Met-Car species in which up to five titanium atoms are replaced by "dopant" zirconium metal atoms.[10] Direct laser vaporization of mixtures of titanium carbide with yttrium, niobium, tantalum, molybdenum, and tungsten does not yield binary metal Met-Car mass spectra of the same intensity or degree of substitution as that observed for zirconium. However, the group IVA mixed metal system $Ti_xHf_yC_{12}$ does show a degree of substitution[10] similar to that observed for the systems reported here. We have varied the mixing ratios of the titanium carbide powder and the powders of the group IIIA, VA, and VIA metals over a wide range in order to determine the maximum extent of substitution achievable upon vaporization of these mixtures, but we have not observed similar propensities for mixing in these systems as in the Ti/Zr case. Furthermore, the systematic variation of the mixing ratios to optimize production of the Met-Car species was undertaken to try to circumvent the overwhelming abundance of metal-oxide clusters produced, particularly upon vaporization of the mixtures rich in the metals yttrium and tungsten. The spectra shown here represent the maximum degree of substitution achievable for each system studied, where vaporization experiments were performed on mixtures with compositions ranging from being 30 times richer in the carbide to 4 times richer in the pure metal.

It is intriguing to observe Met-Car species in which one metal is replaced by other metals that heretofore have shown no propensity to assemble into the Met-Car structure. Furthermore, the substitution of one metal by others of different groups suggests that it may actually be possible to "tailor" the electronic properties of these clusters. Recently, Rantala et al.[12] pointed out that substitution of a vanadium atom for a titanium atom in the neutral Ti_8C_{12} should stabilize the cluster because of the additional nuclear charge, while replacement of a titanium by the group IIIA scandium should slightly destabilize the cluster. As we recently discussed,[7] it is likely that both ionic and neutral M_8C_{12} species are forming upon vaporization, and the observed limited extent to which yttrium replaces titanium atoms is consistent with Rantala et al.'s prediction.[12] However, the observation of weak mass spectral intensities for $Ti_7Y_1C_{12}^+$ and $Ti_6Y_2C_{12}^+$ contradicts the recent proposal of Lin and Hall,[13] which implies an enhancement in the stability of both the $Ti_7Y_1C_{12}^+$ (from ion/molecule reactions) and the $Ti_6Y_2C_{12}^+$ (from the ionization of $Ti_6Y_2C_{12}$ by hot electrons) species.[7] As the $Ti_7Y_1C_{12}^+$ and

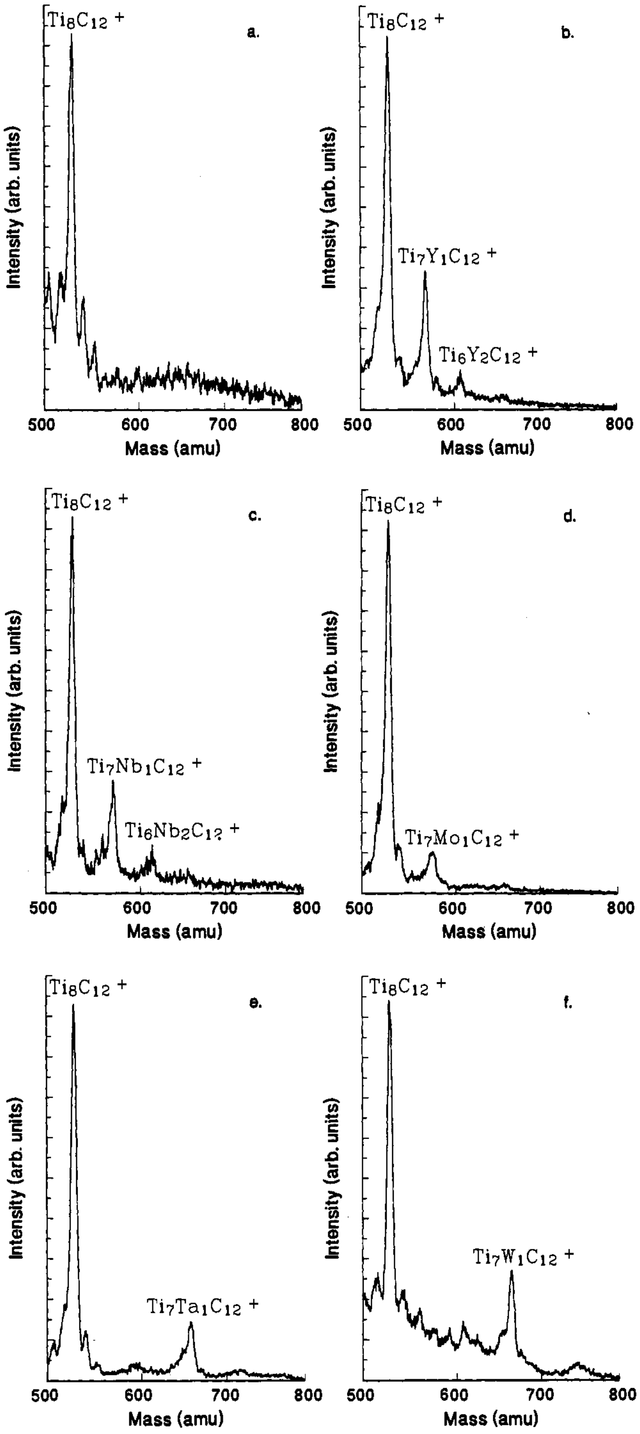

Figure 1. (a) High-mass range of a mass spectrum obtained from the direct laser vaporization of pure TiC. (b-f) Mass spectra obtained from the direct laser vaporization of mixtures of TiC and Y, Nb, Mo, Ta, and W, respectively.

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$Ti_6Y_2C_{12}$ species both have the magic number of 18 metal electrons, we would expect them to be evidence by more intense "magic" peaks in the mass spectrum. Analogous to Rantala et al.'s predicted effect for vanadium,[12] the group VA (Nb, Ta) and VIA (Mo, W) metals would be expected to stabilize the Met-Car system due to their higher nuclear charge. However, as we noted earlier, these systems also display weak mass spectral intensities and a limited degree of substitution relative to the zirconium-substituted system, indicating that the substitution of titanium by metals with greater nuclear charge may not stabilize the cluster.

Whether the extent to which another metal atom can be incorporated in the structure of a "pure" Met-Car is a kinetic, steric, or electronic effect is an intriguing question. We have varied the metal:metal ratio of our target mixtures without appreciably affecting the degree of substitution. Steric effects are unlikely to be the influencing factor, as Nb, Ta, Mo, and W are all smaller than Zr due to greater nuclear charge and the lanthanide contraction, but show a significantly lower degree of substitution in the titanium Met-Car than does zirconium. Finally, the model which has been used to predict boron- and nitrogen-doped fullerene stabilities[14] would predict a destabilizing effect for yttrium, which does manifest itself here in an observed weak $Ti_7Y_1C_{12}^+$ intensity and low degree of substitution, in accord with the prediction for scandium.[12] However, if one applies the effect predicted for vanadium to the Nb, Ta, Mo, and W systems, our findings are counterintuitive to this theory. Furthermore, these metals display substitution patterns (albeit with weaker intensity) similar to that of hafnium, which is isovalent with zirconium.

Central to our investigation into the production of binary metal metallocarbohedrenes is understanding the stabilities, structure, and electronic nature of these species. Defining the range of systems which can assemble into the Met-Car structure is the first step in determining their properties. The range of metals which we have thus far observed to form binary metal Met-Cars, with their differing size, electronic nature, and coordination character, is the prelude to a more complete understanding of these systems. Presently, our group has begun to study the production of these binary metal metallocarbohedrene species in a laser-induced plasma source similar to that originally used to generate Met-Cars[6] and to investigate their stabilities, reactivities, and dissociative nature. Along with these experiments, further modeling of these mixed metal systems could elucidate the factors responsible for the observations reported here as well as shed further light on the structure and symmetry of these clusters.

Note Added in Proof: Additional investigations with a different technique in our laboratory have shown that the $Ti_xTa_yC_{12}^+$ system manifests a further degree of substitution than that observed in the present work.[15] However, for all conditions studied the $Ti_xY_yC_{12}^+$ system shows only a limited degree of substitution, consistent with the results reported here.

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