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# Photodissociation of Metallo-Carbohedrene ("Met-Cars") Cluster Cations

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Castleman and co-workers have recently reported the formation of especially stable metal–carbon clusters designated "metallo-carbohedrenes", or "met–cars".[1-4] In their work, metal–carbon mixed clusters having the formula $M_8C_{12}$ form preferentially from plasmas containing a carbon precursor and transition metals (e.g., $Ti_8C_{12}$, $V_8C_{12}$). A structure consisting of a pentagonal dodecahedron with $T_h$ symmetry has been proposed for these clusters. Additional experiments detect the formation of larger zirconium met–cars clusters whose structures are suggested to be multiple dodecahedron cages.[3] Theoretical investigations have focused on an explanation for the unusual stability of these systems.[7,8] We have recently observed that met–cars clusters also exist in chromium, molybdenum, and iron analogs.[9] However, there are no experimental measurements other than mass spectra to provide insight into the structure and bonding of these various cluster systems. We report here the first mass-selected photodissociation experiments on met–cars clusters. These experiments reveal the decomposition mechanism of these species and provide new insight into their bonding and stabilities.

Met–cars clusters are produced with a laser induced plasma reactor like that described by Castleman.[5,6] Cluster cations formed in the condensation process are mass-selected and laser-excited in a reflectron time-of-flight mass spectrometer system, which provides mass analysis of the resulting fragment ions.[10]

Figure 1 shows the photodissociation mass spectrum of titanium and zirconium met–cars clusters. In each case the $M_8C_{12}^+$ species has been mass-selected and then excited with the second harmonic of a Nd:YAG laser (532 nm). The data are plotted with a computer difference technique, where the depletion of the parent ion mass appears as a negative peak and fragment ions are indicated with positive peaks. The laser for these experiments is unfocused with a pulse energy of approximately 20 mJ/pulse. Preliminary power dependent studies indicate that dissociation is probably not a one-photon process. Additionally, the fragmentation patterns observed are essentially unchanged when an excimer laser (308 nm) is used for excitation.

The titanium spectrum contains the 5/12 (i.e., $Ti_5C_{12}$), 6/12, and 7/12 fragment ions, suggesting that decomposition occurs bya sequence of neutral metal atom losses. The ionized metal atom is also observed as a fragment. The observation of both charged met–cars fragments and charged metal atoms indicates that the ionization potentials of these two species are nearly the same. Vanadium, chromium, and iron met–cars cations follow the same pattern of sequential metal atom loss observed here, and they also form the corresponding $M^+$ fragment. However, under the same laser power conditions used for titanium and vanadium, iron and chromium analogs lose up to six and seven metal atoms, respectively.

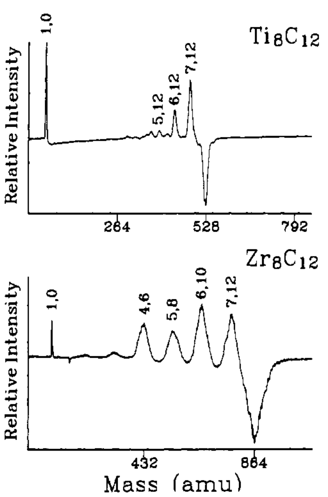

**Figure 1.** Photodissociation mass spectra for the cluster ions $Ti_8C_{12}^+$ and $Zr_8C_{12}^+$ at 532 nm. The negative peaks represent depletion of the mass-selected parent ion, while the positive peaks represent the fragment ions. The titanium cluster loses a series of metal atoms, while the zirconium cluster loses $M–C_2$ units.

Investigations of the bonding in met–cars systems suggest that the dodecahedron structure provides a metal–carbon network with special stability.[7,8] In the picture of Lin and Hall,[7] the role of the transition metals in this structure is to relieve strain and link strongly bound C═C units through M—C $\sigma$ bonds. This bonding is expected to be important primarily for the early transition metals. d electron repulsion with the C═C $\pi$ electrons becomes more important as the d shell is more highly occupied, which weakens the $M–C_2$ interaction. Met–cars clusters should therefore be less stable for the later transition metals. Our results here support this stability trend. Chromium and iron met–cars systems, which are expected to be more weakly bound, fragment much more extensively than titanium or vanadium analogs.

The behavior of the zirconium met–cars cluster, however, is qualitatively different from that of the other metals. Prominent fragment ions are 7/12, 6/10, 5/8, 4/6, and the $Zr^+$ peak, suggesting that decomposition occurs by an initial loss of a metal atom followed by $Zr–C_2$ elimination steps. Castleman has suggested that these met–cars clusters grow by the successive addition of $M–C_2$ units.[1-3] The importance of M—(C═C) interactions has also been suggested by Lin and Hall.[7] The decomposition of the zirconium system here seems to be consistent with these schemes. Lin and Hall also suggest that M—(C═C) $\sigma$ bonding is much weaker than the C═C bonds. The decomposition by successive loss of metal atoms, which is illustrated by the majority of these systems, could also be consistent with this same scenario. It would seem, however, that the M—(C═C) interactions in the zirconium system are stronger than those for the other metals.

These photodissociation experiments indicate that there are at least two general mechanisms important in met–cars cluster decomposition, metal atom elimination and $M–C_2$ elimination. Chromium and iron met–cars clusters are suggested to be less stable overall than titanium and vanadium systems, while the $M–C_2$ interactions are suggested to be especially strong for

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zirconium met–cars clusters. While it is tempting to attach structural significance to these differences, the different dissociation patterns observed here do not require that there be different cluster structures. Bonding strength variations are also sufficient to explain the behavior observed. However, it will be interesting to see if these results are understandable in the context of detailed bonding theory on these systems.

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