Metallo–Carbohedrenes: Chromium, Iron, and Molybdenum Analogues

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Abstract: The formation of especially stable metal–carbon clusters, which have been designated metallo–carbohedrenes by Castleman and co-workers, has previously been reported for the early transition metals (Ti, Zr, Hf, V). Clusters having the formula M_8C_{12} were recognized as especially stable species which were formed in plasmas containing the metal and a carbon-containing precursor. A similar laser induced plasma technique is employed to synthesize chromium, molybdenum, and iron analogues of these so-called "met–cars" clusters and to study their photodissociation behavior. These observations suggest that met–cars cluster formation is a more general phenomenon than previously recognized. While chromium and molybdenum form the "super-magic" 8/12 stoichiometry efficiently, met–cars formation competes with other special stoichiometries in the iron clusters. Implications for the bonding properties in met–cars systems are discussed.

Introduction

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 clusters with the formula M_8C_{12} are formed preferentially from plasmas containing carbon and transition metals (e.g., Ti_8C_{12}, V_8C_{12}). These clusters are believed to have special stability, and a structure consisting of a pentagonal dodecahedron with T_h symmetry has been proposed. In the case of the zirconium met–cars system, larger clusters are observed which are proposed to have structures consisting of multiple connected cages.[3] Recent theoretical investigations focus on an explanation for the unusual stability of these systems.[5–8] In experiments to date, met–cars formation has been reported only for certain early transition metals (Ti, V, Zr, Hf).[1–4,9,10] We report here the first observation of met–cars clusters containing chromium, iron, and molybdenum. These data suggest that met–cars formation in more general than previously recognized, and they provide further insight into the bonding in these novel systems. The recent report of the isolation of Ti_8C_{12} lends further interest into this fascinating area of met–cars clusters.[11]

Previous investigations of met–cars clusters have focused on the special M_8C_{12} stoichiometry (henceforth 8/12) exhibited in mass spectral distributions and on the ability of these clusters to chemisorb specific numbers of molecular ligands.[1–4] These studies establish that the met–cars clusters have unique structure and bonding properties distinctly different from those of metal–carbon clusters in the metallo–fullerene family.[12–18] In recent studies

from our laboratory, photodissociation experiments have also investigated the novel properties of the titanium, vanadium, and zirconium met–cars systems.[9] In the studies here, both mass spectra and photodissociation mass spectra are examined for metal–carbon clusters containing chromium, iron, and molybdenum. The mass spectra and photodissociation mass spectra are compared to similar data obtained previously for met–cars systems and to those obtained for metallo–fullerenes. The mass distributions and dissociation patterns exhibited are characteristic of the met–cars family of clusters.

Experimental Section

Metal–carbon clusters are generated with a laser plasma reactor like that described by Castleman.[19,20] A rotating rod containing the metal of interest is mounted in a laser vaporization cluster source, and the expansion gas (helium) is seeded with methane or acetylene at a level of about 1%. The vaporization laser is either a XeCl excimer laser (308 nm) or the second harmonic of a Nd:YAG laser (532 nm). Vaporization of the metal sample ignites a plasma, and the hydrocarbon gas dissociates in this plasma. Mixed metal–carbon clusters grow as the plasma is quenched by collisions with excess expansion gas. Cation clusters formed in this process are cooled by the supersonic expansion and probed with a downstream reflectron time-of-flight mass spectrometer (RTOF). For measurements of mass distributions, the cold cation clusters formed in the laser vaporization process are extracted from the molecular beam into the RTOF with pulsed acceleration plates. For measurements of photodissociation mass spectra, the parent ion of interest is mass selected and laser excitation occurs in the turning region of the reflectron field. The photodissociation laser for these experiments is a Nd:YAG laser (532 nm). The flight time through the remaining drift tube section provides mass analysis for the fragment ions. The operation of the RTOF instrument for these photodissociation experiments has been described previously.[21]

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Metallo-Carbohedrenes: Cr, Mo, and Fe Analogues

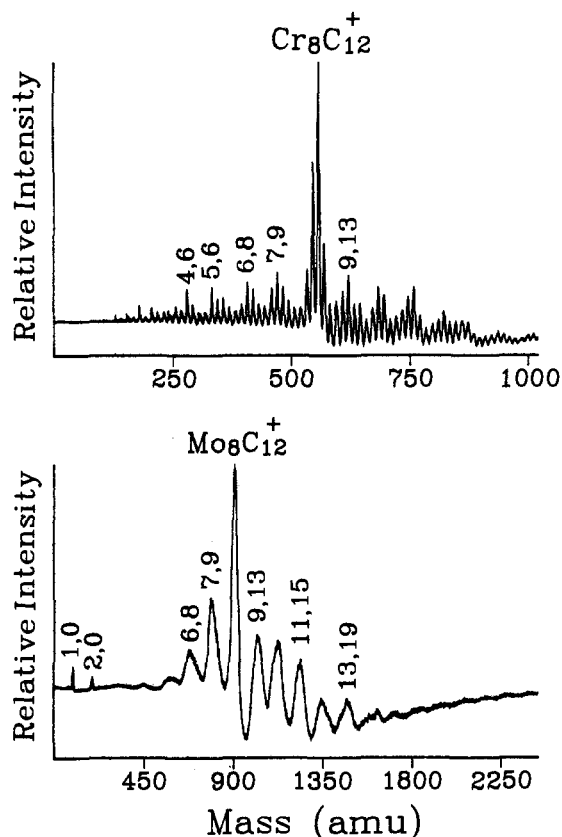J. Am. Chem. Soc., Vol. 115, No. 15, 1993 6959

Figure 1. The mass spectra of cation metal-carbon clusters produced by the laser vaporization of chromium or molybdenum samples in a plasma containing acetylene. As shown, a variety of stoichiometries are produced, but there is preferential formation of the $M_8C_{12}^+$ species for both metals.

Results and Discussion

Figure 1 shows the mass spectra obtained for chromium and molybdenum experiments, indicating the formation of various metal-carbon clusters. The peaks in the molybdenum spectra are broadened by the isotope distribution, while the chromium spectrum exhibits better mass resolution. In both systems the prominent cluster (i.e., the "magic number") is $M_8C_{12}^+$, which is the same as the met-cars stoichiometry reported previously by Castleman. The general contour of the mass distribution observed here is sensitive to the mass spectrometer focussing conditions. However, under all focussing conditions the $M_8C_{12}^+$ peaks are relatively more intense than any of the surrounding peaks. The patterns in these mass spectra are very similar to those observed for titanium, vanadium, zirconium, and hafnium metal-carbon clusters by Castleman and co-workers[1-4] and to our previous data for these early transition metals.[9] The Castleman experiments observed essentially the same mass distributions for neutral clusters detected by photoionization and for cations produced directly in the cluster growth process, while we have only studied the nascent cations. On the basis of these cation mass spectra, then, one would conclude that $Cr_8C_{12}^+$ and $Mo_8C_{12}^+$ are met-cars analogues. Photodissociation experiments described below provide an additional test of this hypothesis.

Figure 2 shows the mass spectrum resulting from a similar experiment on iron. In this system, there is no single magic number species, but the 8/12 stoichiometry is prominent and it is followed by a significant truncation in the spectrum. On the other hand, species such as the 7/8 or 12/12 cluster are equally as prominent as the 8/12 species. On the basis of the mass distribution alone, therefore, it would be difficult to conclude that $Fe_8C_{12}^+$ is an especially stable met-cars cluster. If it is, either the degree of stability compared to other stoichiometries is less or the growth mechanism for iron is more complex and less selective for this
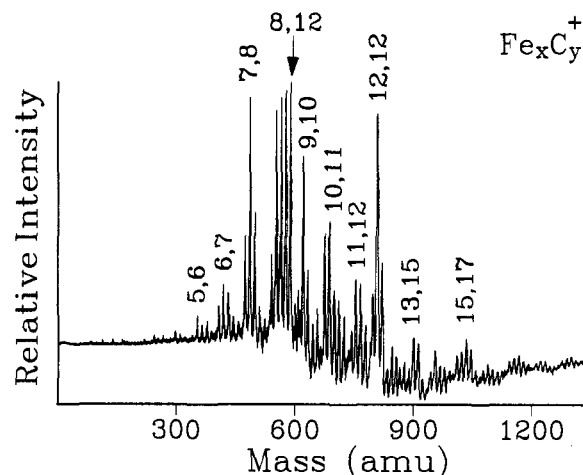

Figure 2. The mass spectrum of metal-carbon cations produced by laser vaporization of iron in a plasma containing acetylene. More varied stoichiometries are produced than for chromium or molybdenum. The $Fe_8C_{12}^+$ peak is followed by a significant loss in intensity, while the $Fe_{12}C_{12}^+$ peak has a significant local maximum in intensity.

stoichiometry. Again, the photodissociation data below provide better insight into these questions.

We have recently studied the photodissociation of titanium, vanadium, and zirconium met-cars systems in our RTOF instrument.[9,10] When mass selected and photodissociated by visible (532 nm) or ultraviolet (308 nm) lasers, $Ti_8C_{12}^+$ and $V_8C_{12}^+$ lose a sequence of three metal atoms.[9] However, $Zr_8C_{12}^+$ dissociates by the sequential loss of neutral MC_2 fragments. None of these clusters exhibit the pattern of C_2 elimination which is found for fullerene clusters. These two fragmentation schemes seem to indicate that there are two subclasses of met-cars systems. We have also been able to produce larger titanium and vanadium metal-carbon clusters which have near 1:1 M:C ratios, i.e., $Ti_{14}C_{13}^+$.[10] These species are believed to have symmetric structures composed of fcc crystal lattice fragments, analogous to the bulk structure of TiC. When larger cluster cations of this type, having compositions of the form $M_xC_y^+$ ($x \geq 8$; $y \geq 12$), are photodissociated, the 8/12 stoichiometry is usually produced as the most abundant photofragment.[10,22] These observations suggest that photodissociation experiments may be useful in identifying other met-cars clusters or obtaining qualitative information about the relative stability of met-cars clusters. We have therefore investigated the photodissociation behavior of the various prominent M/C clusters formed in the mass distributions here.

Figure 3 shows the photodissociation mass spectra for $Cr_8C_{12}^+$ and $Fe_8C_{12}^+$. These spectra are accumulated with a computer difference technique in which the parent ion signal without the dissociation laser is subtracted from the full mass spectrum (parent ion plus fragment ions) with the fragmentation laser on. The resulting spectra have a negative peak at the parent ion mass indicating its depletion and positive peaks at the fragment ion masses. The photodissociation laser used for these experiments is an unfocused Nd:YAG laser operating at 532 nm (photon energy 2.33 eV). The spectrum is observed with an unfocused laser at high pulse energy ($\sim$40 mJ/cm²) at about the same intensity used to study previous met-cars systems.[9] We suspect that the absorption process under these conditions is largely multiphoton in nature.

As indicated in Figure 3, $Cr_8C_{12}^+$ and $Fe_8C_{12}^+$ dissociate by a series of metal atom losses. Photofragment species of the form $M_xC_{12}^+$ are observed for $x = 2-7$. Unfortunately, the fragmentation spectrum is not time-resolved, and so we cannot distinguish

(22) In some systems the $M_8C_{13}^+$ ion is produced as the prominent fragment, suggestive of an endohedral carbon atom in the usual met-cars structure.
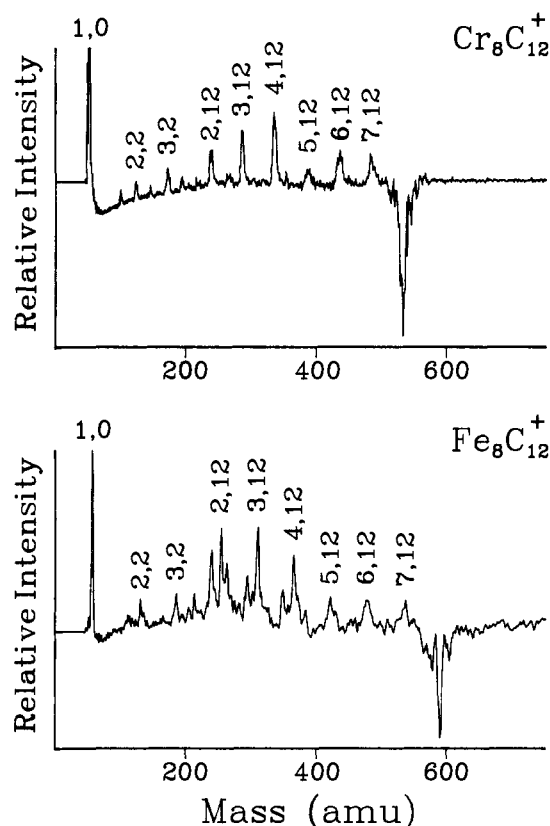
Figure 3. The photodissociation mass spectrum of $Cr_8C_{12}^+$ and $Fe_8C_{12}^+$ at 532 nm. The fragment ions correspond to multiple metal atom loss from the parent ion.

Figure 4. The photodissociation mass spectrum of $Mo_8C_{12}^+$ at 532 nm. The primary product ion corresponds to the loss of MoC_2.

between sequential fragmentation events and concerted loss of multiple atoms. However, knowledge of the exact mechanism is not necessary for recognizing patterns in the dissociation and comparing these to previously studied systems. In the lower mass range, 2/2 and 3/2 fragment ions are observed. Surprisingly, there are virtually no fragment ions containing an intermediate number of carbon atoms (3–11). The atomic metal ion peak is observed here for both systems, which was also observed in the photodissociation of titanium and vanadium 8/12 species. This is attributed to either elimination of the atomic metal ion or reionization of neutral atomic photofragments by the dissociation laser.

The fragmentation pattern of multiple atom loss is the same as that observed previously for $Ti_8C_{12}^+$ and $V_8C_{12}^+$.[9] Thus, the dissociation patterns as well as the mass distributions of these clusters are consistent with the designation of the chromium and iron analogues as members of the met–cars family. However, the *extent* of fragmentation observed here is much greater than that observed for the other met–cars analogs. The titanium and vanadium 8/12 species lose a maximum of three metal atoms, while the species here lose up to six. In both the previous met–cars systems studied (titanium and vanadium) and the present systems (chromium and iron), the absorption process leading to photofragmentation is believed to be multiphoton in nature. Therefore, one explanation for the more extensive fragmentation observed here is that the chromium and iron systems absorb light more efficiently and that they absorb more photons, hence more energy, than the corresponding titanium and vanadium systems at 532 nm. However, the titanium and vanadium analogues were studied at different excitation energies, and the dissociation pattern observed was independent of energy. It seems likely, therefore, that the more extensive fragmentation observed here under similar laser conditions is due to lower bond energies in the chromium and iron analogues compared to the titanium and vanadium systems.
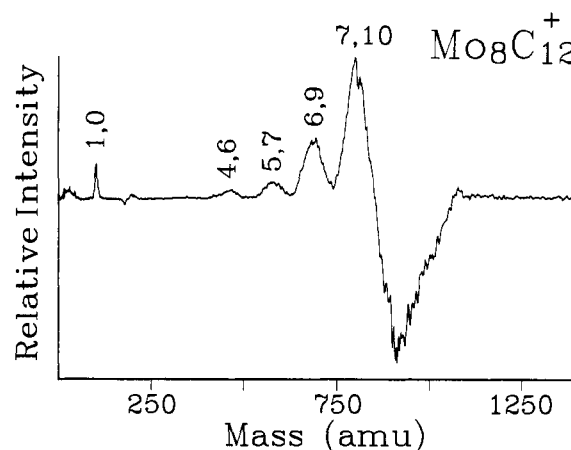
Figure 4 shows the photodissociation mass spectrum observed for $Mo_8C_{12}^+$ under conditions similar to those cited above. The mass peaks are again broad due to the isotope distribution from molybdenum. The fragmentation pattern here is somewhat different from that observed for chromium and iron. The most prominent fragment is the 7/10 peak, which corresponds to the loss of MoC_2 from the parent ion. The second most intense peak corresponds to loss of Mo_2C_3. The MC_2 loss channel was observed previously, as discussed above, for zirconium met–cars clusters. Therefore, the fragmentation pattern here is again consistent with that observed for previous met–cars systems, confirming, along with the mass distribution, that $Mo_8C_{12}^+$ belongs to the met–cars family. The Mo_2C_3 unit, which is lost here but was not observed before, corresponds to the composition of the five-membered rings suspected of forming the dodecahedron structure for these clusters. The 5/7 fragment differs in composition from the main 7/10 one by this same 2/3 decrement, and the smaller 4/6 fragment is also less than the 6/9 unit by this same decrement. Therefore, the loss of MC_2 and/or M_2C_3 units, either in sequential or concerted fashion, is suggested by this fragmentation pattern. Interestingly, of the several systems now studied, only zirconium and molybdenum clusters exhibit the apparent loss of fragments of the form M_xC_y. All the other first row metal systems lose primarily metal atoms. This may be indicative of a general difference in metal–carbon bonding between the first row and second row elements.

As an additional probe of the structures and decomposition patterns in these systems, we have photodissociated the $Fe_{12}C_{12}^+$ species. This cluster has a 1:1 metal–carbon ratio like the fcc nanocrystal systems we have studied previously for larger titanium and vanadium carbon clusters.[10] In those systems, dissociation of the larger clusters produced either the 8/12 stoichiometry or the 8/13 stoichiometry as the primary photofragments.[10] Figure 5 shows that similar behavior applies here. The main photofragment from the 12/12 parent ion is the 8/12 met–cars stoichiometry. Thus, while the initial mass distributions do not single out the $Fe_8C_{12}^+$ cluster, it is the most abundant photofragment in the decomposition of larger species.

Overall, the combined measurements described here of mass distributions and photodissociation patterns indicate that the chromium, iron, and molybdenum clusters with carbon have many of the same properties as the met–cars clusters described previously. We therefore conclude that these systems are also met–cars analogs and that they probably will have the dodecahedron structure proposed for the 8/12 stoichiometry. The mass distributions observed here, especially for iron, seem to indicate that the tendency to form the special 8/12 stoichiometry is less for these middle transition species than it is for the early transition metals. The fragmentation patterns for the species here, with the possible exception of the molybdenum analogue, are more
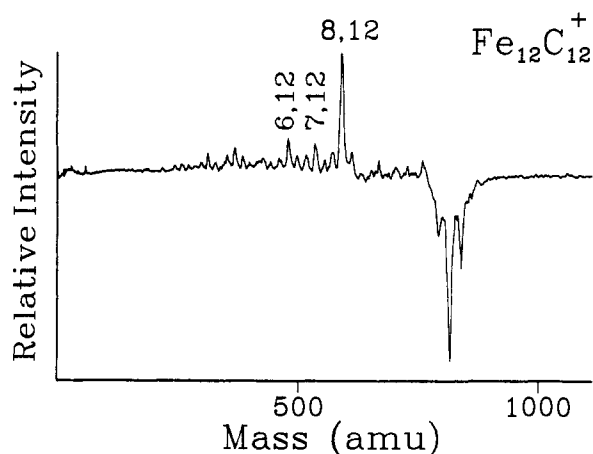
Figure 5. The photodissociation mass spectrum of $Fe_{12}C_{12}^+$ at 532 nm. $Fe_8C_{12}^+$ is the main fragment ion.

extensive than those observed previously. These combined data indicate in a very qualitative way that the mid-transition metal met–cars systems may be less stable than their early transition metal counterparts.

Investigations of the bonding in met–cars systems suggest that the dodecahedron structure provides a metal–carbon network with special stability.[5–8] In the picture of Lin and Hall,[5] the role of the transition metals in this structure is to relieve strain and link strongly bound C=C units through M—C σ bonds. The metal atoms have a 4+ oxidation state balancing the formal 4–

charge of (C=C). The 4+ oxidation state is prominent for the early transition metals and becomes less important as the d shell is more highly occupied, suggesting that met–cars clusters should exist, but be less stable, for the later transition metals. Our results here support this general stability trend, but they suggest that additional attention may need to be paid to possible differences in metal–carbon bonding between the first and second row metals.

Our results here suggest that met–cars cluster formation is more pervasive than previously recognized. Other second and third row mid-transition metals will probably also form these structures. If the present trend continues, we expect that the bonding in the mid-transition metal species may be somewhat weaker than the bonding in the early transition metal analogues and that there will be some limit in the d orbital occupancy above which met–cars formation is no longer likely. Recent theoretical calculations suggest this same trend, finding that Fe_8C_{12} and Co_8C_{12} are significantly less stable than Ti_8C_{12} and V_8C_{12}. However, the iron and cobalt met–cars clusters are still predicted to be quite stable on an absolute scale, with a bonding energy of 5.5 eV per atom compared to that of 6.1 eV per atom for Ti_8C_{12}.[8] Additional experimental studies to confirm the structures, energetics, and bonding properties of these novel clusters would be extremely valuable.