Reactivities of Metallo−Carbohedrenes: Evidence That $V_8C_{12}^+$ Has T_d or D_{2d} Symmetry

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Received August 14, 1995[⊗]

Abstract: The metallo−carbohedrene $V_8C_{12}^+$ is studied using a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer coupled to a compact supersonic source. Its reactions with water, ammonia, ROH (R = CH_3, C_2H_5, C_3H_7, C_4H_9), and CH_3X (X = Cl, Br, I) are reported. For polar molecules, sequential attachment reactions occur leading to the initial buildup of the product $V_8C_{12}L_4^+$. $V_8C_{12}L_{5-7}^+$ peaks for ammonia and alcohols are also observed, but they grow in slowly. These results provide evidence that the geometric structure of $V_8C_{12}^+$ is the theoretically calculated more stable T_d or D_{2d} symmetry with two sets of metals, as opposed to the T_h symmetry with all eight equivalent metals. In reactions with methyl halide, CH_3X (X = Cl, Br, I), $V_8C_{12}^+$ undergoes four sequential halide abstraction reactions, exclusively, yielding mass spectra that truncate sharply at $V_8C_{12}X_4^+$. Dehydrogenation is observed for the secondary reactions with water and alcohols, ROH (R = H, alkyl), yielding $V_8C_{12}(OR)_2^+$ intermediates. The results from this study are compared to those of other met-cars.

1. Introduction

Since the report of their discovery by Castleman and co-workers in early 1992, metallo−carbohedrenes or "met-cars" with stoichiometry M_8C_{12} (M = Ti, V, Zr, Hf, Cr, Mo, and Fe)[1−8] have become the focus of intense investigation. Like the fullerenes, the met-cars are of fundamental interest and hold promise as important new materials. Several structures have been proposed to account for the special stability of these met-cars.[9−22] A pentagonal dodecahedron cage structure with T_h symmetry was originally proposed[1−5] while, more recently, distorted structures such as T_d and D_{2d}[9,11−13,15−19] have been calculated in some cases to be substantially more stable. Rohmer et al., for example, estimated that the T_d and D_{2d} structures of $Ti_8C_{12}^+$ are more stable than the T_h structure by 190 and 154 kcal/mol, respectively.[19] Structural information has been derived indirectly using various mass spectroscopic techniques. Bowers and co-workers, for example, obtained evidence for a hollow cage structure for $Ti_8C_{12}^+$ using elegant ion "chromatography" experiments.[23] While their experiments provided support for the T_h structure, however, the T_d and D_{2d} structures could not be unambiguously ruled out.

The ion−molecule chemistry of these metal−carbon clusters can also yield insight into their structures. Castleman and co-workers, for example, have found that $Ti_8C_{12}^+$ sequentially associates with up to eight polar molecules such as water, ammonia, methanol, and 2-butanol and up to 4 π-bonding molecules such as C_6H_6, CH_3CN, and C_2H_4.[8,24] From these "titration" reactions, they reasoned that the polar molecules must attach to eight similar metal sites while the π-bonding molecules form surface complexes, with each ligand bound to two metal atoms in a pentagonal ring. All of these results are consistent with the symmetric T_h structure. They have also suggested that the maximum number of iodine atoms abstracted in sequential reactions with CH_3I is related to the number of unpaired electrons on the cluster.[20] Thus, the observation that $Ti_8C_{12}^+$ abstracts one iodine atom, $Ti_7NbC_{12}^+$ four iodine atoms, and $Nb_8C_{12}^+$ five iodine atoms from methyl iodide indicates that these ions contain 1, 4, and 5 unpaired electrons, respectively.

We recently reported the reactions of $V_8C_{12}^+$ with O_2, H_2O, CH_3CN, and benzene in which the latter three reagents were observed to react with this met-car up to 4 times.[21] For example, CH_3CN was observed to clearly truncate at $V_8C_{12}(CH_3CN)_4^+$, with no additional attachments observed. We took this as evidence for the T_d or D_{2d} structure which has two types of metal sites consisting of 4 metal atoms each, as opposed to the eight equivalent metal sites in the T_h structure. These results

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

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have turned out to be somewhat ambiguous, however, since CH_3CN like benzene is capable of bonding in a π fashion to 2 vanadium atoms in a pentagonal face. Nevertheless, since this argument does not apply to the reactions with H_2O, additional studies were warranted. Thus, in this paper we extend our investigation on $V_8C_{12}^+$ to include a wider variety of polar reagents including $C_nH_{2n+1}OH$ ($n = 1-4$) and CH_3X (X = Cl, Br, I). Studies with water and ammonia are also included. The results are consistent with our original assignment that $V_8C_{12}^+$ has T_d or D_{2d} symmetry with two sets of metal sites consisting of four metal atoms each. Either a clear truncation is observed after attaching four ligands or, when additional ligands are added, they do so more slowly than the first four.

2. Experimental Section

All of the experiments were performed on an Extrel FTMS-2000 dual cell Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer[25,26] combined with a compact supersonic source developed by Smalley and co-workers.[27] Laser desorption using the second harmonic of a Nd:YAG laser (532 nm) was used to generate the vanadium−carbon clusters in a manner similar to Castleman and co-workers by seeding the He expansion gas with ~5% methane.[5,28] Reagents were introduced at a static pressure ($10^{-8}-10^{-6}$ Torr) using Varian leak valves or pulsed into the vacuum chamber using General Valve Corporation Series 9 solenoid pulsed valves.[29] Ar was used as the collision gas at a static pressure of ~2×10^{-5} Torr. An uncalibrated Bayard-Alpert ionization gauge was used to monitor pressure. Ion isolation[25] and collision-induced dissociation (CID)[30] were accomplished either by standard FT-ICR radio frequency pulses of variable frequency and power or by using SWIFT excitation.[31]

3. Results and Discussion

A. Reactivity with Water. $V_8C_{12}^+$ is observed to react with a trace background of water (~0.6×10^{-8} Torr) in the ICR cell, as shown in Figure 1, by an initial association of H_2O. Reaction with a second water proceeds by elimination of H_2 yielding, presumably, $V_8C_{12}(OH)_2^+$. Weiller et al. have suggested that a concerted mechanism is operative in the decomposition reaction of water with bare iron clusters involving hydrogen molecule loss.[32] By analogy, two water molecules on adjacent metal atoms of $V_8C_{12}^+$ may interact, each losing one hydrogen atom, to release a hydrogen molecule without hydrogen atoms actually binding to the metal atoms. However, $V_8C_{12}(OH)_2^+$ then reacts further to coordinate an additional two water molecules to yield $V_8C_{12}(OH)_2(H_2O)_2^+$, as shown in Figure 1. The fact that elimination of H_2 to generate $V_8C_{12}(OH)_4^+$ is not observed tends to rule out the concerted mechanism since, presumably, the second two waters should be adjacent to each other in the same way as the first two. In any event the two OH groups on $V_8C_{12}(OH)_2^+$ reduce by two the number of unpaired electrons, having a dramatic effect on its chemistry.

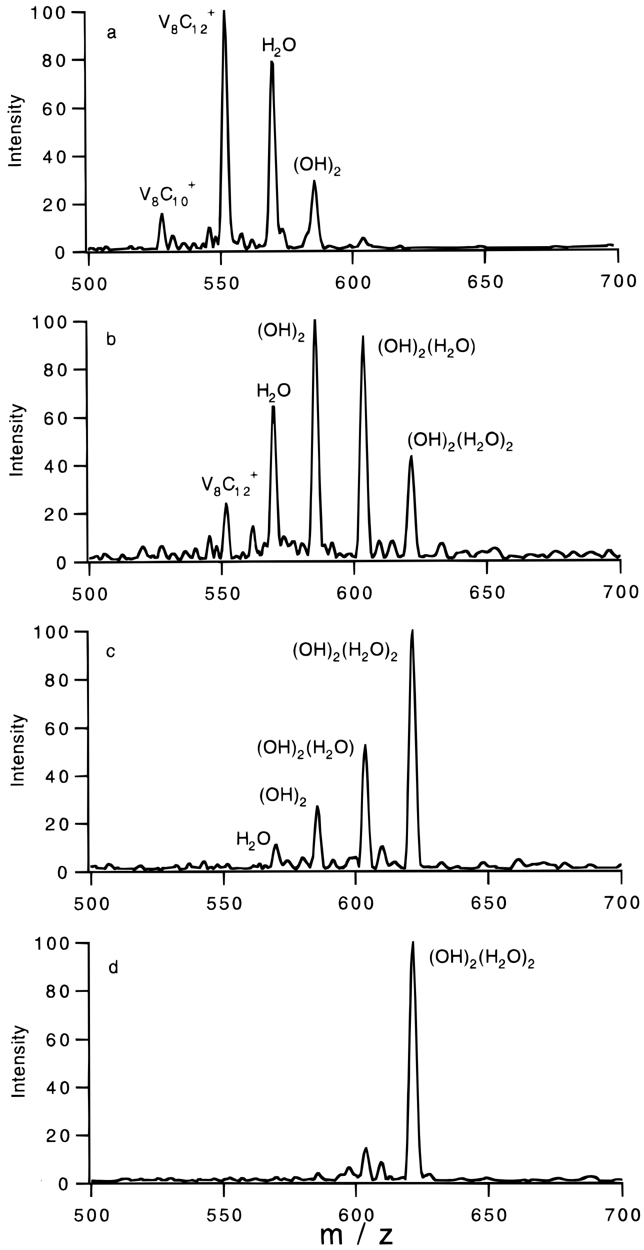

Figure 1. Reaction of $V_8C_{12}^+$ with H_2O (~0.7×10^{-8} Torr). The reaction products correspond to $V_8C_{12}^+$−L, L as labeled on the spectra at various reaction times: (a) 2 s; (b) 6 s; (c) 10 s; (d) 14 s.

Two competitive pathways were found for the reactions of $Nb_4C_4^+$ with H_2O and CH_3OH which are dependent on the pressure of the background argon cooling gas.[33] The pathway for the cooled $Nb_4C_4^+$ is attachment of the first solvent molecule followed by the elimination of H_2 upon reaction with the second solvent molecule to form $(OH)_2$ and $(OCH_3)_2$ adducts, respectively. In the absence of argon cooling gas, however, initial OH or OCH_3 abstraction occurs followed by sequential addition of H_2O or CH_3OH. In contrast, there is only one pathway for $V_8C_{12}^+$ either with or without argon cooling gas. In agreement with the results from our preliminary report,[21] Figure 1 shows that the sequential reactions terminate at $V_8C_{12}(OH)_2(H_2O)_2^+$. This ion remained inert even when the reaction time was increased to 40 s and the pressure of the water was increased up to ~3.9×10^{-8} Torr. Under these conditions, some collisional cooling occurs and attachment of additional waters should have been observed if the eight metals were equivalent.

B. Reactivity with Ammonia. Figure 2 displays spectra obtained by reacting $V_8C_{12}^+$ with NH_3 at ~2.4×10^{-8} Torr.

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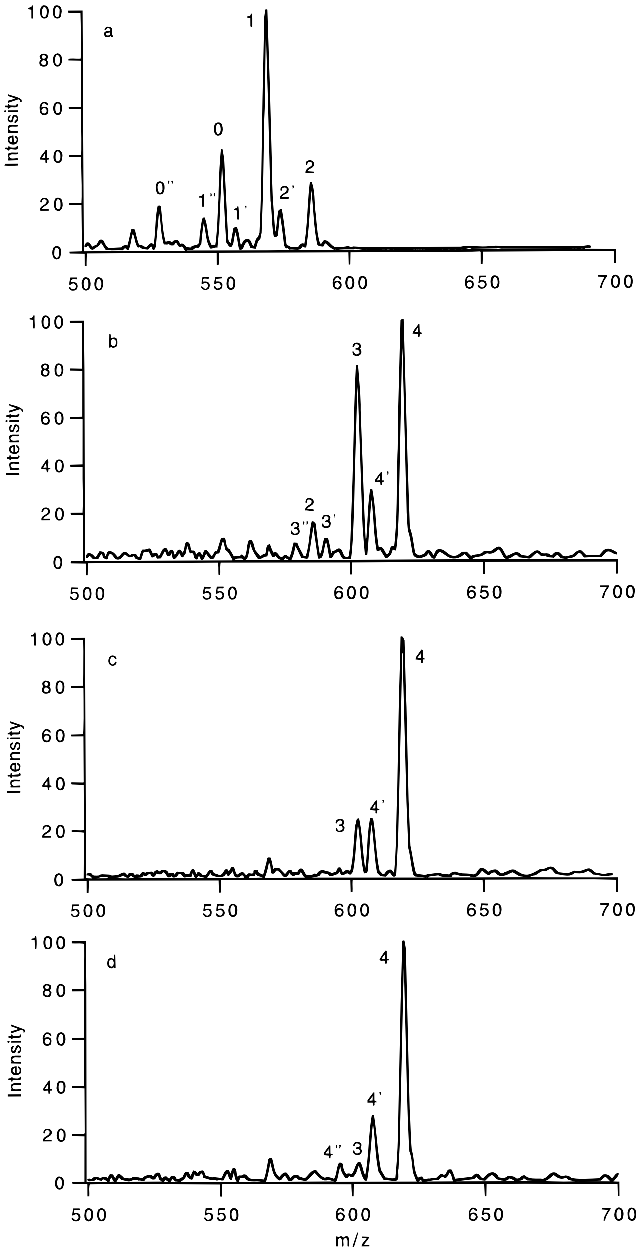

Figure 2. Reaction of $V_8C_{12}^+$ with NH_3 (∼2.4 × 10^{-8} Torr). The numbers correspond to the number of NH_3 attached to $V_8C_{12}^+$ (unprimed), $V_8C_{11}^+$ (primed), and $V_8C_{10}^+$ (double primed) at various reaction times: (a) 1 s; (b) 4 s; (c) 5 s; (d) 6 s.

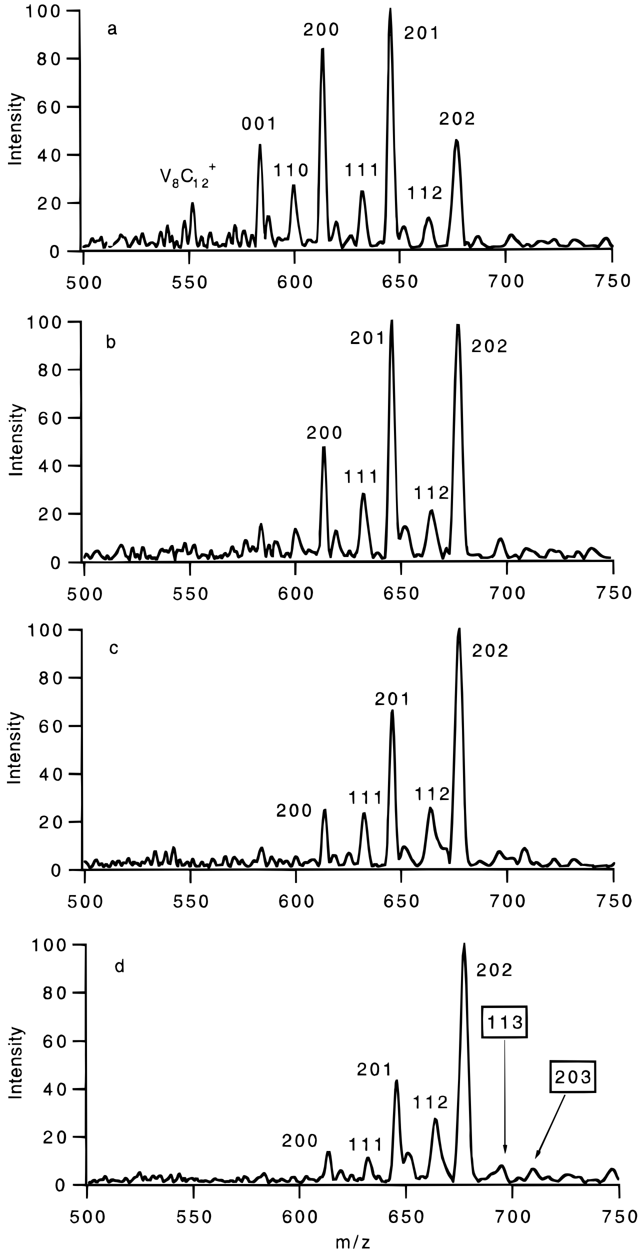

Figure 3. Reaction of $V_8C_{12}^+$ with CH_3OH (∼2.9 × 10^{-8} Torr). The numbers correspond to the number of OCH_3, OH, and CH_3OH attached to $V_8C_{12}^+$ at various reaction times: (a) 1.1 s; (b) 1.5 s; (c) 1.7 s; (d) 2 s. Arrows mark "missing peaks" (see text).

Complicating this study was the presence of trace amounts of O_2. As previously reported,[21] $V_8C_{12}^+$ reacts readily with a static background pressure of oxygen at ∼10^{-8} Torr to generate $V_8C_{10}^+$ and $V_8C_{11}^+$, as well as other ionic products and presumably CO and CO_2 molecules.

$V_8C_{10-12}^+$ undergo sequential association reactions (reaction 1) with ammonia, exclusively, yielding mass spectra that truncate sharply at $V_8C_{10-12}(NH_3)_4^+$, as shown in Figure 2.

$$V_8C_{10-12}(NH_3)_n^+ + NH_3 \rightarrow V_8C_{10-12}(NH_3)_{n+1}^+ \qquad (1)$$

$$n = 0-3$$

When the reaction time was increased to 48 s, $V_8C_{11-12}(NH_3)_5^+$ and $V_8C_{11-12}(NH_3)_6^+$ peaks were also observed to grow in slowly. Castleman and co-workers have shown that $V_8C_{12}^+$ can coordinate as many as 8 ND_3 molecules,[2] but $V_8C_{12}(NH_3)_8^+$ was not observed in our experiments due to the lower pressures. In contrast to water, no dehydrogenation was observed for the reactions with ammonia.

C. Reactivity with Alcohol. In analogy to the reactions with water, methanol, ethanol, 1-propanol, and 2-butanol are also observed to react with $V_8C_{12}^+$ by an initial addition of alcohol, as shown in Figures 3 and 4. Reaction with the second alcohol proceeds by elimination of H_2 yielding, presumably, $V_8C_{12}(OR)_2^+$ ($R = C_nH_{2n+1}$, $n = 1-4$). The dialkoxide ions then react further to attach two more alcohols. The products shift to and truncate at $V_8C_{12}(OR)_2(ROH)_2^+$. Higher order peaks such as $V_8C_{12}(OR)_2(ROH)_{3-5}^+$ are also observed, as shown in Figure 5, but they grow in more slowly. In other words, the first four reactions of each of the alcohols with $V_8C_{12}^+$ are relatively fast while subsequent reactions are slower. As seen in Figure 5, there is a trend toward increasing rates with increasing size of the alcohols. The presence of trace amounts of background moisture in the ICR cell is evidenced by the observation of the combination products $V_8C_{12}(OR)(OH)$-

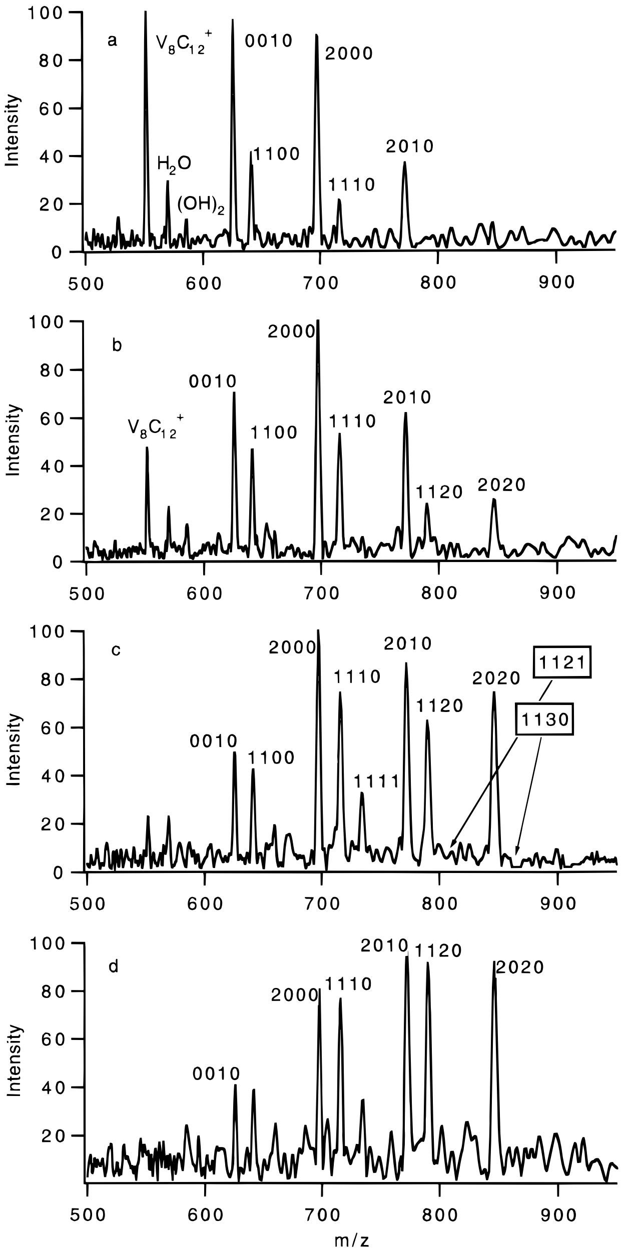

Figure 4. Reaction of $V_8C_{12}^+$ with 2-butanol ($\sim 2.4 \times 10^{-8}$ Torr). The numbers correspond to the number of 2-butoxide, OH, 2-butanol, and H_2O attached to $V_8C_{12}^+$ at various reaction times: (a) 1.5 s; (b) 2.1 s; (c) 2.8 s; (d) 3.2 s. Arrows mark "missing peaks" (see text).

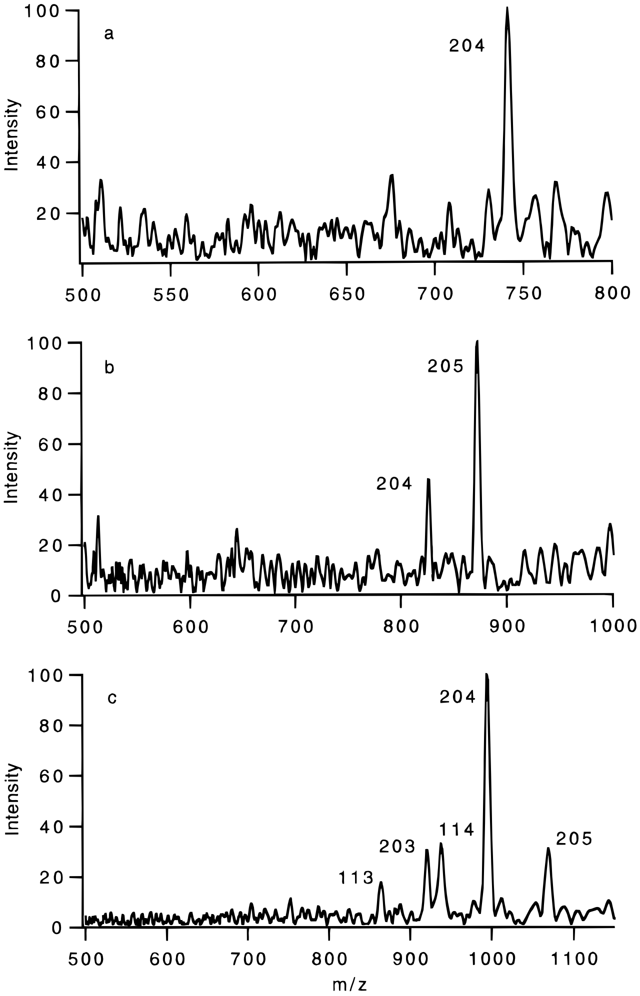

Figure 5. Slow reactions of $V_8C_{12}^+$ with alcohols observed at extended trapping times. The numbers correspond to the number of RO, OH, and ROH attached to $V_8C_{12}^+$ with (a) CH_3OH, taken from the same data set as Figure 3, reaction time (24 s); (b) C_2H_5OH (taken from the same data set as Figure e4, reaction time (20 s)), and (c) 2-butanol (taken from the same data set as Figure 6, reaction time (10 s)).

$(ROH)_{1,2}^+$. Particularly striking in Figures 3 and 4 is the absence of combination peaks containing a total of five ligands. The arrows in the figures denote where these products would have been observed.

D. Reactivities with CH_3X (X = Cl, Br, I). The reactions of $V_8C_{12}^+$ with the methyl halides yield sequential abstraction products, reaction 2, exclusively. The mass spectra shown in Figures 6 and 7 were obtained after cooled $V_8C_{12}^+$ was isolated and allowed to react with CH_3Cl and CH_3I, respectively, introduced through a pulsed valve or a leak valve into the ICR cell. In each case, the reaction products truncate at $V_8C_{12}(X)_4^+$.

$$V_8C_{12}X_n^+ + CH_3X \rightarrow V_8C_{12}X_{n+1}^+ + CH_3 \qquad (2)$$

$$n = 0-3, \qquad X = Cl, Br, I$$

A competitive reaction of $V_8C_{12}(I)_{1-3}^+$ with the trace water present in the ICR cell was also observed, reaction 3. Under these conditions, as shown in Figure 7, truncation occurs at $V_8C_{12}(I)_3(H_2O)^+$ and $V_8C_{12}(I)_4^+$.

$$V_8C_{12}(I)_n^+ + H_2O \rightarrow V_8C_{12}(I)_n(H_2O)^+ \qquad (3)$$

$$n = 1-3$$

The total number of valence electrons for $V_8C_{12}^+$ is 87. Thus, there is an odd number of unpaired electrons for this system, unlike $Ti_7NbC_{12}^+$ which has a total of 80 valence electrons and possibly has an even number of unpaired electrons, as evidenced by the abstraction of four iodine atoms from methyl iodide.[20] Interestingly, $V_8C_{12}^+$ sequentially abstracts only four iodine atoms from methyl iodide even at longer reaction time (15 s) and higher pressure ($\sim 7.9 \times 10^{-8}$ Torr) compared to $Nb_8C_{12}^+$, which abstracts five iodines in its reactions with CH_3I.[20,34] If we presume that $V_8C_{12}^+$, like $Nb_8C_{12}^+$, has at least five unpaired electrons, then the results can be rationalized by having four of the unpaired electrons localized onto the four outer metals in the T_d or D_{2d} structure that are involved in iodine abstraction. The remaining one or more unpaired electrons could be localized onto the four inner metals and less reactive. V and Nb are isoelectronic, but the 3d electrons on V and the 4d electrons on Nb might result in different electronic and geometric structures for these two met-cars. As shown in Figure 7 and mentioned

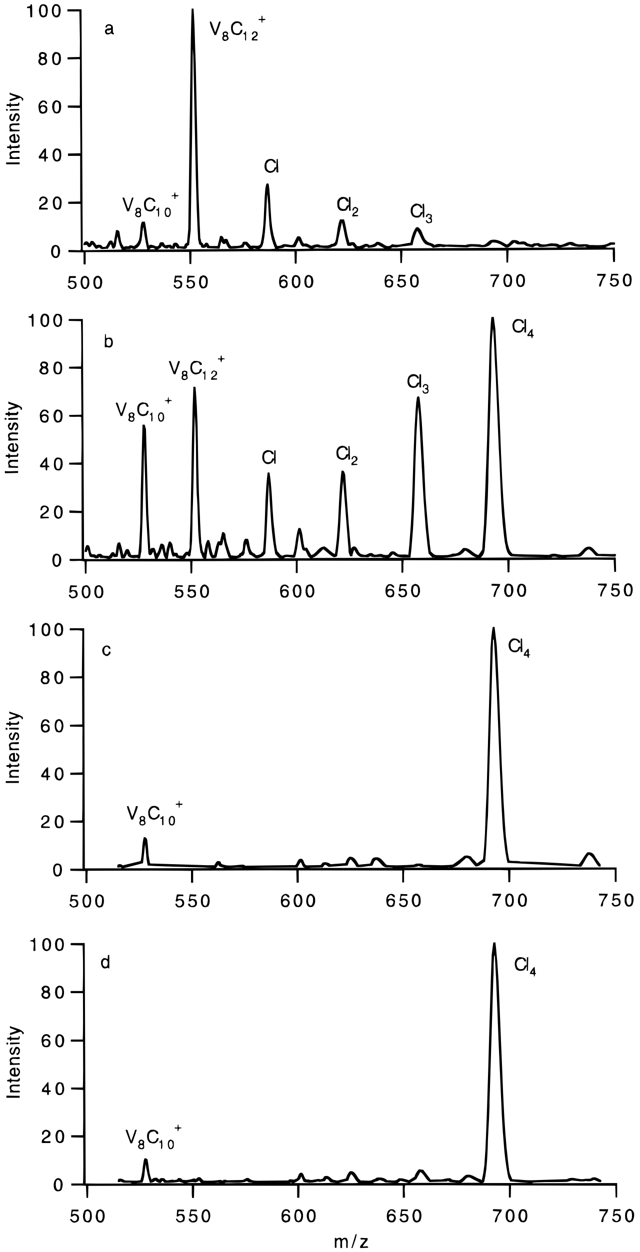

Figure 6. Reaction of $V_8C_{12}^+$ with CH_3Cl introduced through a pulsed valve. The reaction products correspond to $V_8C_{12}^+{-}L$, L as labeled on the spectra at various reaction times: (a) 40 ms; (b) 60 ms; (c) 100 ms; (d) 120 ms.

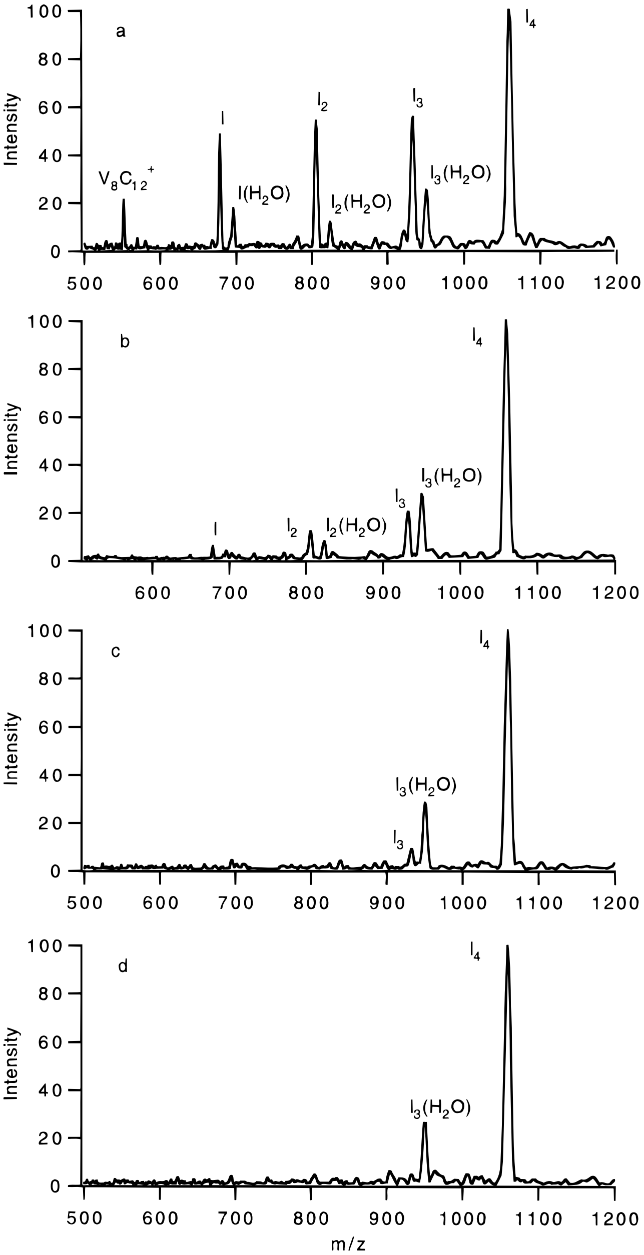

Figure 7. Reaction of $V_8C_{12}^+$ with CH_3I (~3.9×10^{-8} Torr). The reaction products correspond to $V_8C_{12}^+{-}L$, L as labeled on the spectra at various reaction times: (a) 1.5 s; (b) 2 s; (c) 3.5 s; (d) 4 s.

above, $V_8C_{12}(I)_3(H_2O)^+$ is unreactive with H_2O and CH_3I. If the unpaired electrons are evenly delocalized over the eight metals, $V_8C_{12}(I)_3(H_2O)^+$ should react with these reagents to yield association (possibly with dehydrogenation) or abstraction products such as $V_8C_{12}(I)_3(H_2O)_2^+$, $V_8C_{12}(I)_3(OH)_2^+$, or $V_8C_{12}(I)_4(H_2O)^+$. These species, however, are not observed even at longer reaction time (15 s). Similarly, $V_8C_{12}(I)_4^+$ does not react with background water to produce $V_8C_{12}(I)_4(H_2O)^+$.

4. Conclusions

In all of our experiments to date on $V_8C_{12}^+$ involving polar and π-bonding ligands, either a clear truncation is observed after attaching four ligands or, when additional ligands are added, they do so more slowly than the first four. These results provide strong support for the theoretically proposed lower energy T_d or D_{2d} structure. In studies on $Ti_8C_{12}^+$ with 2-butanol, however, Castleman and co-workers saw eight attachments occurring at roughly the same rate with no noticeable buildup of $Ti_8C_{12}L_4^+$, L = 2-butanol, supportive of the T_h structure.[24] It is not necessarily the case that all of the met-cars should have the same structure. The electronic structure and, therefore, the reactivity of $V_8C_{12}^+$ are quite different from that of $Ti_8C_{12}^+$, with $V_8C_{12}^+$ abstracting four iodines and $Ti_8C_{12}^+$ abstracting one from CH_3I[20] and dehydrogenation occurring in the secondary reactions of $V_8C_{12}^+$ with ROH (R = H, alkyl), but not in the analogous reactions of $Ti_8C_{12}^+$. Thus, the geometry of these two met-cars may also be somewhat different.

Alternatively, one significant difference in the experiments performed in this work compared to that of Castleman and co-workers is that considerably lower pressures are utilized in the FT-ICR spectrometer, three or more orders of magnitude lower. Under these conditions, association complexes must be relatively long-lived in order to be radiatively or collisionally stabilized, such that they are observed. Thus, strong binding sites may readily be distinguished from weak binding sites on a cluster, if the latter leads to association complexes which do not survive long enough to be observed. In contrast, at the higher pressures employed in Castleman's experiments, even though the metal sites may not be equivalent, all eight can bind ligands with sufficient strength to be efficiently stabilized by collisions. Therefore, the low-pressure FT-ICR experiments should be better at discriminating more subtle differences in binding site energies, which appears to be the case for these met-cars.

Another possible explanation for the observed sharp truncation at $V_8C_{12}L_4^+$ is that after the first four ligands occupy the four diagonal positions of the met-car, the subsequent ligands could face strong repulsion from the first four, reducing the rate of their attachment. If this were the case, however, the effect should increase with increasing ligand size. In fact we observe the opposite trend. A more dramatic effect is seen for water than for butanol. Thus, we rule out this possibility.

While more systems need to be studied, there seems to be a trend that the amount of dehydrogenation in the ROH reactions is proportional to the number of *accessible* unpaired electrons on the met-car as determined by the iodine abstraction reactions. For example, no dehydrogenation is observed in the reactions of $Ti_8C_{12}^+$ with ROH,[24] one dehydrogenation is observed for $V_8C_{12}^+$ yielding $V_8C_{12}(OR)_2^+$, and two dehydrogenations have been observed for $Nb_8C_{12}^+$ yielding $Nb_8C_{12}(OR)_4^+$.[34] Based on the number of iodine abstractions from CH_3I, $Nb_8C_{12}^+$ has five unpaired electrons, $V_8C_{12}^+$ has four, and $Ti_8C_{12}^+$ has only one. Note also that $V_8C_{12}(OR)_2^+$ which, presumably, has two *accessible* unpaired electrons does not undergo additional dehydrogenation reactions with ROH molecules. $Nb_8C_{12}(OR)_2^+$, on the other hand, presumably has three unpaired electrons and does react with ROH molecules to undergo dehydrogenation.[34]

While dehydrogenation reduces by two the number of unpaired electrons on $V_8C_{12}^+$, it is also conceivable that the RO ligands in essence change the symmetry of the met-car yielding an apparent truncation at four ligands. A similar effect has been reported by Castleman and co-workers on the iodine abstraction product $Ti_8C_{12}I^+$,[24] where attachment of the I reduced the symmetry of the eight metals down to two groups of four metals. In this case a buildup at $Ti_8C_{12}I(ROH)_4^+$ was observed in the distribution leading ultimately to the formation of $Ti_8C_{12}I(ROH)_7^+$. While certainly the presence of the RO group on $V_8C_{12}(OR)_2^+$ has an effect on the local electronic structure at the metals, this is not a problem with NH_3 where a truncation at $V_8C_{12}(NH_3)_4^+$ was observed. In addition unlike CH_3CN, NH_3 is strictly a σ-bonding polar ligand. A related complication, however, would be if the heat released by attachment of, for example, NH_3 would cause a rearrangement of the met-car. While this cannot be completely ruled out, we believe that it is unlikely. In particular, according to the theory discussed above, the distorted structures are lower in energy by as much as 190 kcal/mol. Thus, with increasing internal energy, rearrangement to the more symmetric T_h structure should occur, and this is not observed.

Generally, if there is more than one degenerate highest occupied orbital in a cluster and there is an odd number of unpaired electrons, then this cluster is likely to distort to achieve a more stable geometric structure.[35] Since $M_8C_{12}^+$ (M = Ti, V, Nb) should all have an odd number of unpaired electrons, it is favorable for these met-cars to distort from a T_h structure to a T_d or D_{2d} structure. The previous studies on $Ti_8C_{12}^+$ indicate that only a very small (if any), undetectable distortion from T_h symmetry occurs, while the results presented here suggest that $V_8C_{12}^+$ (and $Nb_8C_{12}^+$)[34] distort to a T_d or D_{2d} symmetry. Some of the trends described above are being further tested on other met-cars and metal−carbon clusters.

Acknowledgment is made to the National Science Foundation (CHE-9224476) for supporting this research.

JA952787C

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