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Multiple-Decker Sandwich Poly-Ferrocene Clusters

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Since the discovery of ferrocene, Fe(η^5-C_5H_5)$_2$ (or $FeCp_2$ for short), in 1951,[1] organometallic compounds have been a subject of many studies in the past several decade. Numerous derivatives of $FeCp_2$ have been synthesized, and some of them have been utilized as catalysts.[2] In related work, a few reports on the synthesis of triple-decker sandwich complexes composed of transition metal atoms and Cp ligands such as $Ni_2Cp_3^+$ (in bulk)[3] and $Fe_2Cp_3^+$ (in gas phase)[4] have been known, and these reports have attracted much attention for detailed study of metal−metal interactions in organometallic systems. Interestingly, it has been shown that the one-dimensional compounds can exhibit semiconducting or even conducting properties in the solid state.[5,6] Recently, we have produced a series of novel organometallic clusters[7] such as M−C_6H_6,[8] M−C_{60},[9] (M = Sc, Ti, V) and Ln−C_8H_8[10] (Ln = lanthanide metals) in the gas phase by a combination of laser vaporization and molecular beam methods, and have shown that they can form multiple-decker sandwich structures in which the metal atoms and the ligand molecules are alternately stacked. In these studies, the organic ligands have been restricted to stable molecules because they could be prepared as a vapor precursor. It is expected that radical ligands such as Cp can make organometallic clusters more stable because the radical ligands can interact with the metal atom more strongly than molecular ligands such as C_6H_6 and C_{60}. However, it is generally difficult to prepare only the radical ligand itself in the gas phase, because it is unfeasible to dissociate a precursor molecule uniquely into the corresponding radical without any contamination.

In recent work, we have developed a new method for the laser vaporization of an organometallic sample containing radical ligands. The laser vaporization method makes it possible to prepare the constituents in considerable density in a short time, and moreover the gas-phase reaction has no interference from solvents, aggregation phenomena, and counterions. The methodology has successfully produced novel gas-phase organometallic clusters composed of ferrocene molecules and transition metal atoms, and has made it possible to include radical ligands in the clusters. Although ferrocene is known as a very stable complex which satisfies the 18-electron rule, ferrocene molecules can surprisingly generate multi-decker sandwich clusters with a connecting transition metal atom. This communication focuses on the formation and the characterization of the one-dimensional poly-ferrocene expressed as $V_n(FeCp_2)_{n+1}$ [$n = 1−3$] by the use of two-laser vaporization, chemical probe, and photoionization methods.

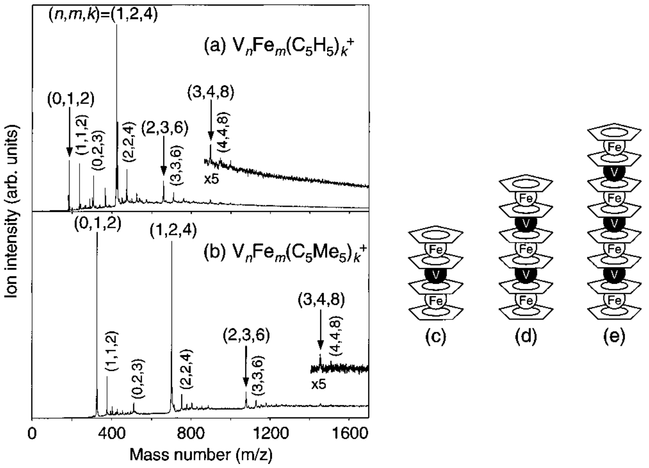

Figure 1. Time-of-flight mass spectra of (a) V−Fe(C_5H_5)$_2$ and (b) V−Fe(C_5Me_5)$_2$ (Me = CH_3) cluster cations. Peaks of cluster cations are labeled according to notation (n, m, k), denoting numbers of vanadium atoms (n), iron atoms (m), and C_5H_5 or C_5Me_5 (k). Geometric structures of (n, m, k) = (1, 2, 4), (2, 3, 6), and (3, 4, 8) can be proposed as $V_1(Fe(C_5H_5)_2)_2$, $V_2(Fe(C_5H_5)_2)_3$, and $V_3(Fe(C_5H_5)_2)_4$, shown in (c), (d), and (e).

Details of the experimental setup were previously described elsewhere.[7,9(b)] Briefly, vanadium (V)−ferrocene ($FeCp_2$) mixed clusters were generated by laser vaporization using two pulsed Nd^{3+}:YAG lasers. Each laser was focused onto the two rotating and translating rods (V and $FeCp_2$). The $FeCp_2$ rod was prepared by pressing $FeCp_2$ powder in the same way described previously for C_{60} rods.[9(a)] The mixed hot vapors of V and $FeCp_2$ were cooled with pulsed He carrier gas (5−6 atm stagnation pressure). After the growth of the cluster in a channel, the neutral clusters of $V_nFe_mCp_k$; (n, m, k) were photoionized with an ArF excimer laser (6.42 eV), and mass-analyzed by a reflectron time-of-flight (TOF) mass spectrometer. The cluster cations produced directly from laser vaporization were also mass-analyzed with a pulsed electric acceleration. To obtain information on the structure of the clusters, the chemical probe of adsorption reactivity was examined by the use of a conventional flow-tube reactor.[11] Inside the flow-tube reactor, NH_3 gas was injected in synchronization with the flow of the clusters, and the NH_3 adducts of the $V_nFe_mCp_k$ clusters were also mass-analyzed. In the ionization energy (E_i) measurement, the ionization photon energy was changed at 0.01−0.03 eV intervals in the range of 3.0−5.0 eV, either with an OPO laser pumped by Nd^{3+}:YAG laser or with a dye laser pumped by an XeCl excimer laser. The fluences of both the tunable UV laser and the ArF laser were kept at $\sim$200 μJ/cm^2 to avoid multiphoton processes. The E_i's of the clusters were determined from the final decline of the photoionization efficiency curves or from appearance threshold energy of the photoion.

Figure 1a shows the mass spectrum of $V_nFe_mCp_k^+$ cluster cations produced by the laser vaporization of V and $FeCp_2$ targets. Peaks of the cationic clusters are labeled according to the notation, (n, m, k)$^+$, denoting the number of V atoms (n), Fe atoms (m), and Cp ligands (k). Under these conditions, the contribution of V_n^+ cluster to $V_nFe_mCp_k^+$ formation was negligible because the abundance of the V_n^+ clusters ($n \geq 2$) was less than 1/100 that of the V^+ atoms. The prominent peaks in the mass spectrum correspond to (n, m, k)$^+$ = (0, 1, 2)$^+$, (1, 2, 4)$^+$, (2, 3, 6)$^+$, and (3, 4, 8)$^+$, where the superscript of + indicates the charge state; singly charged cations. These compositions are expressed as (n, n+1, $2n$+2)$^+$; $V_n(FeCp_2)_{n+1}^+$ [$n = 0−4$]. It should be noted that

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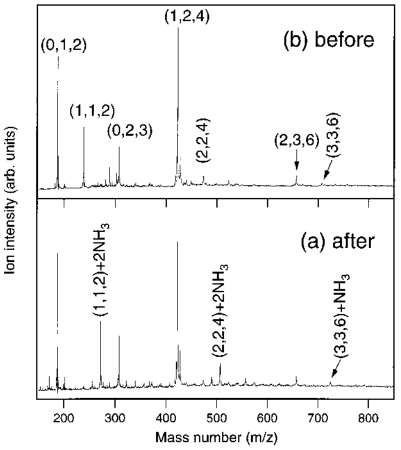

Figure 2. Time-of-flight mass spectra of V−Fe(C_5H_5)$_2$ cluster cations, (a) after and (b) before the reactions with NH_3 reactant [$m = 1-3$]. Peaks of cluster cations are labeled according to notation (n, m, k), denoting numbers of vanadium atoms (n), iron atoms (m), and C_5H_5 (k).

almost no dehydrogenated species produced from $V_n(FeCp_2)_{n+1}^+$ were observed in the mass spectra.

Some experimental conditions were varied in order to deduce the structure. When only the $FeCp_2$ rod was vaporized, $FeCp_2^+$ was prominently observed together with minor peaks of $Fe_2Cp_3^+$, and $Fe_3Cp_4^+$. When the vapor of V atoms was mixed with the $FeCp_2$ vaporization, the V−Fe−Cp clusters were produced additionally at $(n, m, k)^+ = (1, 2, 4)^+$, $(2, 3, 6)^+$, and $(3, 4, 8)^+$, in which the number of $FeCp_2$ molecules was always one more than that of V atoms. The mass distribution of the prominent clusters remained unchanged even when the concentration of V atoms was increased with higher laser fluence for the V rod. These results indicate that (1) laser vaporization of the ferrocene rod can generate vapors of $FeCp_2$ and (2) V atoms link the $FeCp_2$ molecules, resulting in the $V_n(FeCp_2)_{n+1}^+$ clusters. Indeed, the number of the Cp ligand, k, is almost always an even-number, and no metal-switching products were observed; for $k = 4$, for example, only $(1, 2, 4)^+$ was observed and $(2, 1, 4)^+$ and $(3, 0, 4)^+$ were missing.

Figure 2 shows the mass spectra of $V_nFe_mCp_k^+$ cluster cations (a) after and (b) before the reaction with NH_3 gas. Both $FeCp_2^+$ itself and $V_n(FeCp_2)_{n+1}^+$ were unreactive toward NH_3, while the other $V_n(FeCp_2)_m^+$ species drastically diminished with the injection of NH_3, resulting in the formation of their NH_3 adducts. Since it is reasonably presumed that an exterior V atom in $V_n(FeCp_2)_m^+$ would act as a reaction site toward NH_3 molecules, no reactivity of $V_n(FeCp_2)_{n+1}^+$ toward NH_3 clearly indicates that each V atom is sandwiched by $FeCp_2$ molecules.

As described previously,[8] $V_n(C_6H_6)_{n+1}$ clusters also preferably take multiple-decker sandwich structures in which V atoms and C_6H_6 molecules are alternately piled up and the structure has been ascertained by ion-mobility measurements.[12] They are observed as main products in the mass spectrum and show no reactivity toward any gas reactants. By analogy with these facts, it is most likely that the abundant and stable $V_n(FeCp_2)_{n+1}^+$ clusters have multiple-decker sandwich structures; i.e., one-dimensional "polyferrocene", as shown in Figure 1c−e, where the V atoms and the $FeCp_2$ molecules are alternately piled up. Likewise, similar patterns in the mass spectra were observed for Ti−$FeCp_2$ cluster cations. Although it is also conceivable that a central core of vanadium clusters is capped by ferrocene molecules, the missing of $V_3(FeCp_2)_3^+$ on the mass spectrum strongly suggests that the stable $V_n(FeCp_2)_{n+1}^+$ clusters have not the metal core structure but the multiple-decker sandwich one.

The ionization energy (E_i) of $V_n(FeCp_2)_{n+1}$ was measured with the photoionization spectroscopy along with that of V−Fe(η^5-$C_5(CH_3)_5)_2$ (or $FeCp^*_2$ for short). As well as V−$FeCp_2$ cluster cations, V−$FeCp^*_2$ cluster cations show almost the same behavior on the mass spectrum (see Figure 1b); $V_n(FeCp^*_2)_{n+1}^+$ are produced abundantly and they are also nonreactive toward NH_3. The E_i values of the V−$FeCp_2$ and the V−$FeCp^*_2$ clusters are tabulated in Table 1. The E_i value of $V_2(FeCp_2)_3$ could not be determined due to its poor intensity. The E_i values of both $V_1(FeCp_2)_2$ and $V_1(FeCp^*_2)_2$ are much lower than the E_i values of the V atom (6.74 eV), $FeCp_2$ (6.88 eV), and $FeCp^*_2$ (5.88 eV).[13] Moreover, the E_i value of $V_2(FeCp^*_2)_3$ is lower than that of $V_1(FeCp^*_2)_2$. As reported previously,[8(a)] the E_i value of the $V_n(C_6H_6)_{n+1}$ sandwich clusters decreases greatly with the number n; 5.75, 4.70, 4.14, and 3.83 eV for $n = 1$, 2, 3, and 4 with the growth of the layered sandwich complexes. The rapid decrease in E_i can be interpreted theoretically as the delocalization of d-electrons along the molecular axis.[7,14] This E_i change is very similar to those of $V_n(FeCp_2)_{n+1}$ and $V_n(FeCp^*_2)_{n+1}$, implying that delocalization of metal d-electrons occurs in these clusters. Since the orbital energies of π (e_1 symmetry) and π^* (e_2 symmetry) are different between C_5H_5 and C_6H_6, the interaction of d−π orbitals can be expected to be changed. As demonstrated in ab initio calculations for $V_n(C_6H_6)_{n+1}$,[14] the theoretical calculation of Koopmans' theorem and ΔDFT/B3LYP[15] with the MIDI basis set[16] including multireference character works well for transition metal-containing systems, and similar calculations to reveal the electronic structures theoretically are in progress in our group. It should be noted that other experimental methods, such as collision induced dissociation or photodissociation experiments and ion mobility measurements, are also very important and good ways to probe structures specifically.

Table 1. Ionization Energies of $V_nFe_m(C_5H_5)_k$ and $V_nFe_m(C_5(CH_3)_5)_k$ Clusters in eV

composition	ionization energy	
(n, m, k)	$V_nFe_m(C_5H_5)_k$	$V_nFe_m(C_5(CH_3)_5)_k$
(0, 1, 2)	6.88[a]	5.88[a]
(1, 2, 4)	4.14(13)[b]	3.39(10)
(2, 3, 6)	−	3.15(11)

[a] Reference 13. [b] 4.14(13) represents 4.14 ± 0.13.

Although $FeCp_2$ and $FeCp^*_2$ are well-known as very stable complexes which satisfies the 18-electron rule, we have found that these ferrocene derivatives can accept exterior atoms, forming the multiple-decker sandwich clusters. Since multiphoton dissociation studies for the organometallic complexes such as $FeCp_2$ and $Fe(CO)_5$ have shown the formation of Fe atoms in electronically excited states and free Cp ligands,[17] it can be possible to prepare the Fe atoms and the Cp radical ligand in a concentrated density by adjusting the wavelength and the power density of the vaporization. The gas-phase preparation of radical ligands would enable us to generate a variety of novel organometallic clusters and would open up new aspects of photochemistry, electron spin chemistry, and catalytic activity.

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