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Formation of Cobalt−C_{60} Clusters: Tricapped $Co(C_{60})_3$ Unit

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Cobalt (Co)−C_{60} mixed clusters were produced by the combination of laser vaporization and molecular beam methods. Cationic $Co_n(C_{60})_m^+$ clusters were produced predominantly with the compositions $(n, m) = (0-1, 1)$, (1, 2), (1, 3), (2−4, 4), and (5, 5). Both mass spectrometry and a chemical probe method have revealed that compositions of (1, 3) and (4, 4) correspond to a tricapped planar structure and a tricapped trigonal pyramid structure, respectively, in which each Co atom is surrounded by three C_{60}.

1. Introduction

Since the discovery of the third form of carbon, there has been extensive research on the properties of the fullerene.[1,2] A great deal of effort has been spent in the past decade on modifying fullerenes by coordinating atoms both inside and outside the cage structures.[3−5] In particular, the finding of superconducting alkali metal fullerides[6−10] stimulated considerable interest, suggesting that new forms of materials and superstructures can be synthesized with important chemical and physical properties. Recently, the formation of fullerene-based organometallic compounds suggests that the fullerenes may prove to be highly versatile ligands due to their intriguing topography and aromaticity.[11−14] Numerous investigations of transition metals and C_{60} have been reported from gas-phase,[15−18] bulk materials,[19−21] and theoretical calculations.[22−26] However, the nature of the metal−fullerene interface has scarcely been revealed.

The gas-phase studies of transition metals and C_{60} (M_T-C_{60}) have been initiated by Freiser and co-workers,[27] concerning the possibility of a transition-metal endohedral complex. Although endohedral M_T-C_{60} complexes have not been realized in the present stage except for group-3 elements, their findings of exohedral M_T-C_{60} indicated the possibility of new kind of M_T-C_{60} materials. Moreover, Martin and co-workers have reported transition-metal-coated C_{60} clusters,[17] and they have found magic numbers of metal atoms derived from a first complete metal layer on C_{60}. Very recently, our experimental study on $V_n(C_{60})_m$ has opened up an area of multi-metal and multi-C_{60} system.[28] In the previous report, $V_n(C_{60})_m$ clusters form a superstructure at $(n, m) = (1, 2)$, (2, 3), (3, 4), and (4, 4), which we call a multiple-dumbbell structure of alternating V atoms and C_{60} molecules.

This paper focuses on the properties Co−C_{60} by use of laser vaporization, chemical probe, and photoionization methods. Another superstructure of $Co_n(C_{60})_m^+$ is found, which can be explained by the formation of a tricapped $Co(C_{60})_3$ unit. The difference in the nature of the metal−fullerene interface will be discussed between Co−C_{60} and V−C_{60}. The rich variety of newly discovered M_T-C_{60} compounds will extend the application of metal atom doping to C_{60}-based materials.

2. Experimental Section

Co−C_{60} clusters, $Co_n(C_{60})_m$ [=(*n*, *m*) hereafter], were produced by the combination of laser vaporization and the molecular beam method. The experimental setup used in this experiment is almost the same one reported previously.[28,29] A C_{60} rod was prepared by pressing purchased C_{60} powder. The cobalt (Co) rod (Nilaco, 99.998%) and the C_{60} rod were independently vaporized by the frequency-doubled output from two Q-switched Nd^{3+}:YAG lasers (532 nm, ∼10 mJ/pulse for Co and ∼100 μJ/pulse for C_{60}). The fluence of laser vaporization for C_{60} was kept low to avoid so-called C_2-loss fragmentation. The vaporized Co atoms and C_{60} were cooled to room temperature with He carrier gas (5−7 atm stagnation pressure) and then grown into Co−C_{60} clusters. After the growth of the clusters in a channel (2-mm diameter and 4-cm length), they were sent into the extraction chamber through a skimmer (3-mm diameter). The neutral clusters were ionized by an ArF excimer laser (6.42 eV), whereas the cluster cations were extracted by applying a pulsed electric potential (∼4 kV) without photoionization. The ions were mass-analyzed by a reflectron time-of-flight (TOF) mass spectrometer. To enhance the sensitivity, for heavy cluster ions, an efficient ion detector known as “Even-Cup” was used,[30] in which cations accelerated to 20 keV hit a cuplike aluminum dynode and the ejected electrons extracted onto a grounded scintillator were converted into photons, which were detected by a photomultiplier. To get further information on the electronic and geometric structures of the clusters, a chemical probe method was employed. $Co_n(C_{60})_m^+$ clusters were reacted with various gases (CO, O_2, C_2H_2, C_2H_4, C_6H_6, and NH_3) by using a conventional flow tube reactor (FTR),[31] which was mounted downstream of the cluster growth channel. The reactant gas diluted by 1 atm He was injected into the FTR synchronously with the Co−C_{60} clusters.

3. Results and Discussion

3.1. Geometrical Structures of $Co_n(C_{60})_m^+$. Figure 1 shows a typical example of a mass spectrum of $Co_n(C_{60})_m^+$ cluster cations produced by the foregoing procedure. Under this condition, the contribution of Co_n^+ clusters to $Co_n(C_{60})_m^+$ formation was negligible because the abundance of the Co_n^+ clusters was less than 1/100 compared to that of Co^+ atoms. Mass peaks of the clusters are labeled according to the notation (*n*, *m*), denoting the number of Co atoms (*n*) and C_{60} (*m*). The

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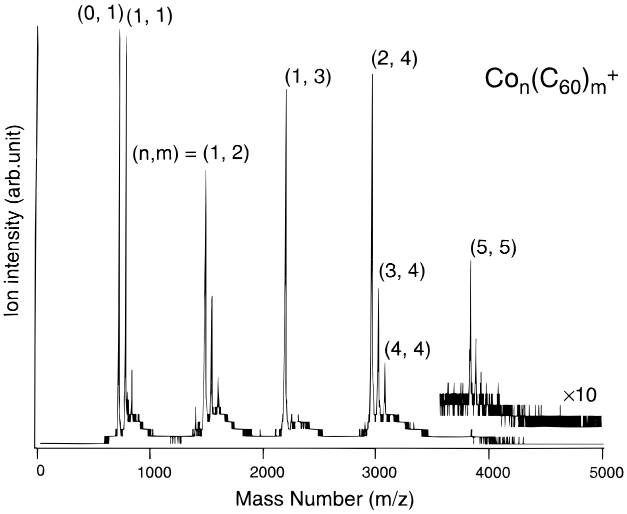

Figure 1. Time-of-flight mass spectrum of cobalt (Co)$-C_{60}$ cations, $Co_n(C_{60})_m{}^+$ ($n = 0-5$, $m = 1-5$).

main peaks in the spectrum are (n, m) = (0$-$1, 1), (1, 2), (1, 3), (2$-$4, 4), and (5, 5) for each m. The pattern in the mass spectrum differs from that of $V_n(C_{60})_m{}^+$, in which (n, n+1) clusters ($n = 1-3$) are prominently abundant due to a chain structure between V atoms and C_{60}. To explain the mass spectrum of $Co_n(C_{60})_m{}^+$, the adsorption reactivity of (1, 3) and (n, 4) was examined by the chemical probe method with various gases.

3.1.a. $Co_1(C_{60})_3{}^+$. $Co_1(C_{60})_3{}^+$ is abundant among species containing a single metal atom, while (1, 3) is missing in the dumbbell $V_n(C_{60})_m{}^+$ clusters.[28] In the chemical probe experiment, $Co_1(C_{60})_3{}^+$ was nonreactive toward all of the gases, such as CO, O_2, C_2H_2, C_2H_4, C_6H_6, and NH_3, whereas quite minor peaks of (n, 3) [$n \geq 2$] showed an occurrence of adsorption reaction into their adduct of (n, 3)+L (L = reactant gases). Because $C_{60}{}^+$ itself is inert for the above gases, it is presumed that the Co atom is blocked by surrounding C_{60}. The adduct formation of (n, 3) [$n \geq 2$] implies that the cluster possesses an exterior Co atom. Therefore, we proposed that (1, 3) takes a tricapped planar structure, as shown in Figure 2a. Looking at the whole mass spectrum in Figure 1, moreover, the series of clusters with $m = 3$ differs markedly from other series of m = 1, 2, 4, and 5; the mass peaks of (n, 3) are clearly truncated at $n = 1$ and are scarcely produced at $n \geq 2$. Since (2, 2) and (2, 4) are observed, it is surprising that (2, 3) is missing. Although neither steric nor electronic effects can explain it, this result is ascribed to the special stability of (1, 3) compared to other (n, 3)'s [$n \geq 2$], and the larger clusters are predominantly fragmented into (1, 3) during the cluster formation.

If (1, 3) takes a tricapped planar structure, (1, 2) should be bent to some extent as a precursor of (1, 3) because the Co atom of (1, 2) in that configuration can afford to attach to the third C_{60}. When (1, 1) and (1, 2) were reacted with CO, they indeed resulted in CO adducts of (1, 1)+3CO and (1, 2)+2CO, respectively. Figure 3 shows the adsorption reaction of $Co(C_{60})_2{}^+$, $Co(C_{60})_1{}^+$, and Co^+ toward CO, in which every set of two spectra is shown on the same intensity scale. Although the clusters reacted with CO without mass selection of the reaction precursor, the total ion intensity in every set seems almost conserved before/after the reactions within experimental uncertainties. Thus, it is reasonably assumed that the adsorption reaction mainly results in the CO adduct formation with negligible fragmentation. Comparison between (1, 2) and (1, 1) shows that the Co atom in (1, 2) is not located on either C_{60}, because a Co atom on C_{60} can bond three CO molecules, as observed in (1, 1). Then, the Co atom in (1, 2) should bridge two C_{60} (Figure 2f). The CO adduct formation shows the Co atom in (1, 2) can bond another molecule, which is consistent with the (1, 3) formation.

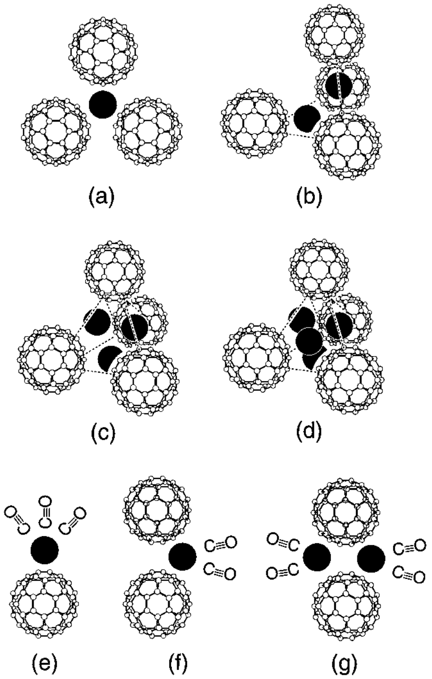

Figure 2. Proposed geometric structures: (a) $Co_1(C_{60})_3{}^+$, (b) $Co_2(C_{60})_4{}^+$, (c) $Co_3(C_{60})_4{}^+$, (d) $Co_4(C_{60})_4{}^+$, (e) $Co_1(C_{60})_1(CO)_3{}^+$, (f) $Co_1(C_{60})_2(CO)_2{}^+$, and (g) $Co_2(C_{60})_2(CO)_4{}^+$.

Furthermore, we examined the adsorption reaction of (1, 2) with C_6H_6, which induces a larger steric hindrance than CO (Figure 4). Although (1, 2) reacted with C_6H_6, the adduct of (1, 2)+C_6H_6 was never produced, but instead (1, 1)+C_6H_6 newly appeared. According to Armentrout and co-workers,[32-34] collision-induced dissociation experiments indicated that the averaged dissociation energy of the $Co^+-C_6H_6$ complex is around 2.2 eV, which is twice that of the Co^+-CO complex. The large difference in the bond energy seemingly explains the dissociation product of (1, 1)+C_6H_6 because (1, 1)+C_6H_6 might be formed by kinetic energy release of C_{60} dissociation due to large binding energy between Co^+ and C_6H_6. As shown in Figure 3a, however, (1, 2) associates with two CO molecules, which causes an almost equivalent thermodynamic effect. Furthermore, (1, 1) undergoes an association reaction with one C_6H_6 molecule, which is impossible if the heat created by the association reaction must be similarly compensated by releasing a C_{60}. Instead, therefore, the reason for the C_{60} release is probably because a Co cation cannot hold two C_{60} and one C_6H_6 simultaneously because of lack of electronic stability. As described later, electron counting to the $Co-C_{60}$ clusters can explain the electronic stability of (1, 1)+C_6H_6 on the basis of the 18 valence electrons (VEs) rule.[35] Then, the reaction seems to be a simple displacement. This result implies that the dissociation energy between Co^+ and C_{60} is lower than that between Co^+ and C_6H_6: $D_0(Co^+-CO) < D_0(Co^+-C_{60}) < D_0(Co^+-C_6H_6)$.

As reported previously, no reaction takes place for the linear dumbbell $V_1(\eta^6\text{-}C_{60})_2{}^+$ toward either CO or C_6H_6.[28] Since the averaged dissociation energies of V^+-CO and $V^+-C_6H_6$ are similar to those of the Co^+ case, the adsorption reaction of $Co(C_{60})_2{}^+$ with CO and C_6H_6 should be attributed not to thermodynamical energetics but to the bent structure. Therefore,

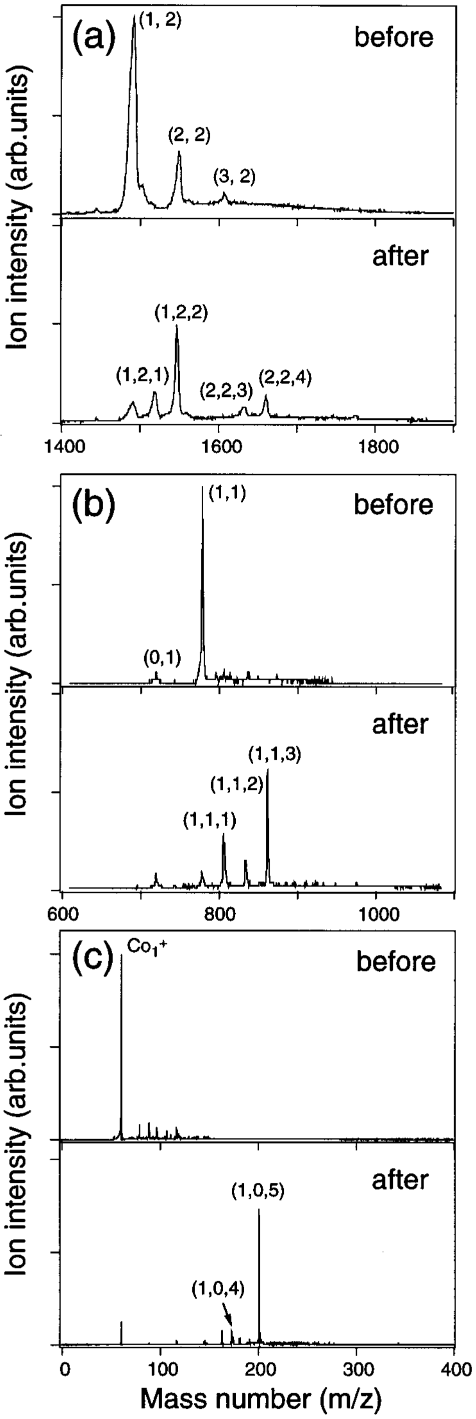

Figure 3. Time-of-flight mass spectra of $Co_n(C_{60})_m^+$ before and after adsorption reaction with CO: (a) $Co_1(C_{60})_1^+$, (b) $Co_1(C_{60})_2^+$ and (c) Co_1^+. The most intense peak in each spectrum before the reaction is normalized. The product compositions are expressed by (*n*, *m*, *k*) for $Co_n(C_{60})_m(CO)_k^+$.

it is concluded that the (1, 2) cluster takes a bent structure, which results in the tricapped planar structure of (1, 3) with the third C_{60}.

It should be noted that (2, 2)+4CO is found as a CO adduct of (2, 2), as shown in Figure 3a. Even though the concentration of CO was increased, the final adduct of (2, 2)+4CO never changed. Since the bridging Co atom in (1, 2) and the exterior Co atom on C_{60} in (1, 1) preferably bond two and three CO molecules (Figure 2f,e), respectively, the (2, 2)+4CO adduct formation reveals that both of the Co atoms in (2, 2) bridge two C_{60}, as shown in Figure 2g. This conclusion is somewhat surprising, because an expected isomer of (2, 2) such as Co−(C_{60})−Co−(C_{60}) never exists in the cluster beam. Then, this result suggests that the laser-vaporized C_{60} may enable metal atoms to move on C_{60} until they find the most stable site. In fact, Wurz et al. have reported[36] that the laser-vaporized C_{60} has an internal temperature of $\geq$2000 K without cooling carrier gas, which is rather higher than one from an oven source ($\sim$500 K). Namely, these superstructures may result from the advantageous combination of laser vaporization of C_{60} and molecular beam methods, opening up a new aspect of metal−fullerene chemistry.

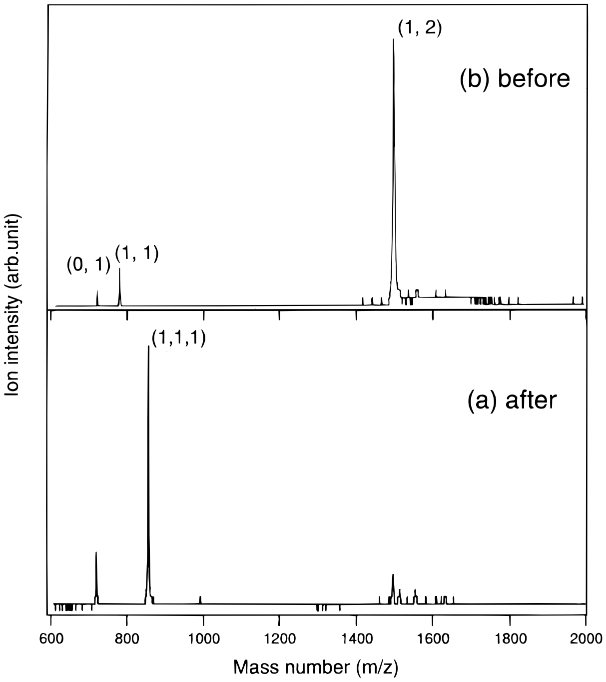

Figure 4. Time-of-flight mass spectra of $Co_1(C_{60})_2^+$, (a) after and (b) before the adsorption reaction toward benzene (C_6H_6; Bz). The product compositions are expressed by (*n*, *m*, *k*) for $Co_n(C_{60})_m(Bz)_k^+$.

3.1.b. $Co_n(C_{60})_4^+$ ($n = 2-4$). To get further information on the clusters having multi-metal atoms, a similar chemical probe experiment was employed for the (*n*, 4) series using reactant gases CO and O_2. A typical example of the reaction toward O_2 is shown in Figure 5. The compositions of (2, 4), (3, 4), and (4, 4) were nonreactive, although (5, 4) and (6, 4) were reactive. This result indicates that (2, 4), (3, 4), and (4, 4) have no exterior Co atom in the clusters, because an exterior Co atom could react with O_2 as discussed above. We also obtained the same reactivity with CO, although the inert reactivity does not directly offer a conclusion about the position of the cobalt atoms or whether the atoms are isolated by C_{60} or cluster with each other. Considering that the Co atom is favorably surrounded by three C_{60}, however, the plausible structures of (2, 4), (3, 4), and (4, 4) can be presumed, as shown in Figure 2b−d. The formation processes of each cluster could be as follows; for (2, 4), the first Co atom surrounded by three C_{60} forms the stable (1, 3), and then the second Co atom forms another local (1, 3) using the fourth C_{60}, which results in a double tricapped plane of (2, 4), as shown in Figure 2b. For (3, 4) and (4, 4), the third and the fourth Co atoms form additional local (1, 3) groups, resulting in the trigonal pyramid shown in Figure 2c,d. In (4, 4), two tetrahedra (trigonal pyramids) of Co_4 and $(C_{60})_4$ form a "composite di-tetrahedral structure" without bonds between Co atoms.

According to Hoffmann et al.,[26] the trigonal pyramid Co_4 cluster is calculated to be stable in bulk C_{60}, in which the four

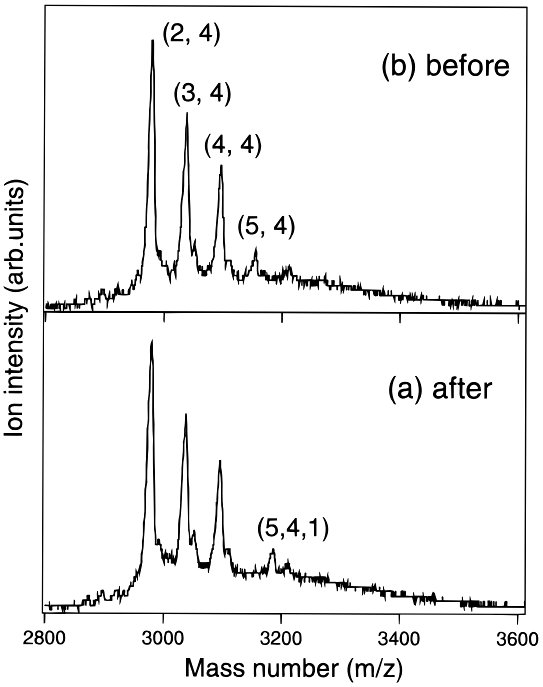

Figure 5. Time-of-flight mass spectra of $Co_n(C_{60})_4^+$, (a) after and (b) before oxidation reactions. The product compositions are expressed by (*n*, *m*, *k*) for $Co_n(C_{60})_m(O_2)_k^+$.

TABLE 1: Allotted Numbers of Valence Electrons (VEs) for C_{60} in $Co_n(C_{60})_m(CO)_k^+$ Clusters on the 18 VEs Rule

	number of VEs in each component			VEs per C_{60}
(*n*, *m*, *k*)	Co^+	*k*(CO)	*m*(C_{60})	(C_{60})/*m*
(1, 1, 3)	8	6	4	4
(1, 2, 2)	8	4	6	3
(1, 3, 0)	8	0	10	3(4)

apexes of the Co_4 cluster point to the outer apexes of a local $(C_{60})_4$ trigonal pyramid in the bulk C_{60} lattice; the trigonal pyramid of Co_4 is inside the trigonal pyramid of $(C_{60})_4$. Then, our proposition for the (4, 4) cluster differs from theirs because the metal−metal bonding is not assumed and the apexes of four Co (not cluster) are located at the center of each $(C_{60})_3$ face. Although either geometry is conceivable, the plausible structure for (4, 4) seems to be our proposed pyramid structure, because the (3, 3) cluster never appears in our mass spectrum. If (4, 4) consists of a Co_4 cluster core at the center as proposed by Hoffmann et al., (3, 3) having a Co_3 cluster core should also be observed in the mass spectrum. The absence of (3, 3) implies that the four Co atoms in (4, 4) are isolated by C_{60}. In the gas phase, it seems reasonable that the different structure for (4, 4) becomes stable because of the lack of packing factors in the lattice.

3.2. Co−C_{60} Bonding Nature. As reported elsewhere,[37] clusters composed of C_{60} and early 3d transition metals (Sc, Ti, and V) take a multiple-dumbbell structure. For Co−C_{60} clusters, however, they take a tricapped structure. To deduce the bonding nature qualitatively, we apply electron counting to the Co−C_{60} clusters, on the basis of the 18-valence-electrons (VEs) rule for organometallic compounds.[35] Chemical probe experiments with CO present information on the electronic structure when each CO ligand is counted as a two-electron donor, together with the eight VEs of the Co^+ atom.

As shown in Figure 3, every cluster of (1, 2), (1, 1), and (1, 0) has a specific maximum number of CO molecules adsorbed (k_{max}). The specific numbers of k_{max} are two, three, and five for (1, 2), (1, 1), and (1, 0), respectively. The number of VEs allotted to C_{60} is listed in Table 1. For (1, 0), five CO molecules completely satisfy the 18-VEs rule, and then the 18 VEs rule predicts that C_{60} donates three and four electrons in (1, 2) and (1, 1), respectively. Similarly, C_{60} donates 3(4) electrons in (1, 3) according to the 18-VEs rule. Although C_{60} consists of five- and six-membered rings, these results clearly show that C_{60} never acts as a η^5- or η^6-ligand in the Co−C_{60} clusters, where the symbol η is conventionally used to signify how many carbon atoms of the ring are bonded to the metal atom. The most likely number of VEs for C_{60} is three in the Co−C_{60} cluster, that is to say, C_{60} acts as a three-electron donor for Co atom. Since in the dumbbell structure of $V_n(C_{60})_m^+$, $Sc_n(C_{60})_m^+$, and $Ti_n(C_{60})_m^+$, C_{60} acts as a six-electron donor,[28,37] the result of the Co−C_{60} clusters implies that the bonding nature of C_{60} depends on metal elements. In fact, Freiser and co-workers observed the formation of $FeC_{60}(CO)_4^+$, instead of $FeC_{60}(CO)_5^+$, as a product of the reaction between C_{60}^+ and $Fe(CO)_5$, which suggests that C_{60} can be either an η^2- or η^3-ligand.[38] These results may indicate that C_{60} molecules ligate either with the hexagonal rings donating only three electrons or with the pentagonal rings, depending on the metal element involved. As pointed out in the preceding section, 3.1.b, the partial ligation of C_{60} reasonably explains the electronic stability of (1, 1)+C_6H_6 as $Co(\eta^3\text{-}C_{60})_1(\eta^6\text{-}C_6H_6)_1$ based on the 18-electron rule.

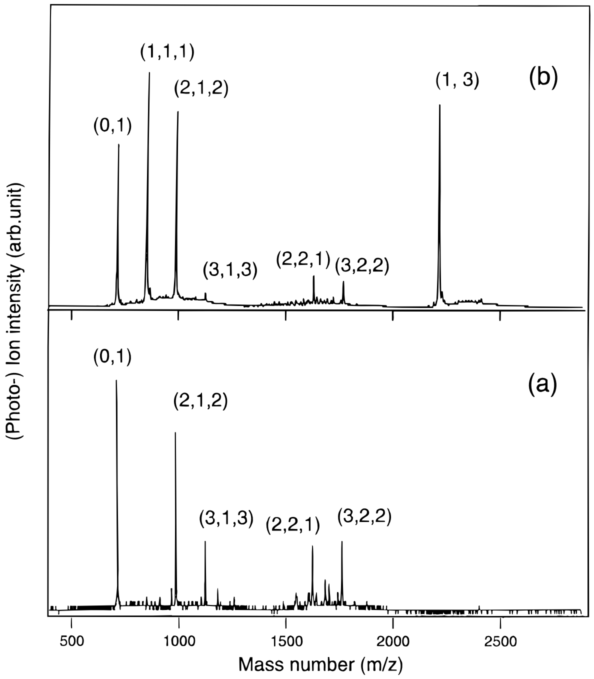

Figure 6. Time-of-flight mass spectra of (a) cationic $Co_n(C_{60})_m(Bz)_k^+$ clusters and (b) photoionized $Co_n(C_{60})_m(Bz)_k$ clusters by a 6.42-eV photon. The product compositions are expressed by (*n*, *m*, *k*) for $Co_n(C_{60})_m(Bz)_k^+$.

According to Lauher et al.,[39] for organometallic sandwich compounds of cyclopentadienyl (η^5) or benzene (η^6), the orientation of aromatic rings is preferably bent above 18 VEs to avoid electronic repulsion. Similar deformation can be expected in Co−C_{60} when the six(five)-membered ring on C_{60} is treated as a localized donor of π electrons. The conceivable bent structure for $Co(C_{60})_2^+$ is indeed consistent with the chemical probe experiment mentioned in the preceding section, but another important factor of ionic bonding should be taken into account because C_{60} can work not only as an electron donor but also as an electron acceptor. A total bonding scheme including all of the molecular orbitals of C_{60} is indispensable to the quantitative understanding of the electronic structures.

3.3. Ionization Energies of $Co_n(C_{60})_m$ Clusters. As reported previously, the ionization energy (E_i) of the metal−C_{60} cluster is a good index to gain a better understanding of d−π interaction. However, no $Co_n(C_{60})_m$ clusters could be ionized by an ArF excimer laser (6.42 eV). Figure 6 shows two mass spectra of (a) cationic $Co_n(C_{60})_m(Bz)_k^+$ clusters and (b) photoionized $Co_n(C_{60})_m(Bz)_k$ clusters, to show that the E_i's of $Co_n(C_{60})_m$ are higher than 6.42 eV. Although the E_i of C_{60} is above the photon energy of the ArF, the photoion of C_{60}^+ was inevitably observed through two-photon absorption probably because of the large amount of neutral C_{60} in the cluster beam. Without benzene, no ions of $Co_n(C_{60})_m^+$ were observed via one-photon ionization of the ArF laser, whereas photoionized product ions with benzene were observed at $(n, m, k) = (2, 1, 2)$, (3, 1, 3), (2, 2, 1), and (3, 2, 2). The E_i of the benzene complex with Co is comparatively low; $E_i = 5.53$ eV for $Co(C_6H_6)_2$.[40] The low E_i of the benzene complex is characteristic of d−π interaction, and the addition of benzene decreases the E_i's of $Co_n(C_{60})_m$. Thus, the high E_i's of the Co−C_{60} clusters imply that the interaction of Co−C_{60} is weaker than that of Co−C_6H_6, especially in cationic states. For Sc−C_{60}, Ti−C_{60}, and V−C_{60},[28,37] in which C_{60} is an η^6-ligand for metal atoms, their E_i's are very low, around 5.8 eV. Therefore, we conclude that C_{60} is not an η^6-ligand in Co−C_{60}. This is consistent with the results of the chemical probe experiments.

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