Photoelectron Spectroscopy of Scandium-Arene Complex Anions

Ken Judai, Yoshiaki Nakamura, Makoto Tachibana, Yuichi Negishi, Atsushi Nakajima,* and Koji Kaya[†]
Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522
[†]Institute for Molecular Science, Myodaiji, Okazaki 444-8585

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Scandium-arene complex anions, $Sc_1(arene)_m^-$ (m = 1, 2; arene = benzene and toluene) were generated by the gas phase reaction of laser vaporized atoms with aromatic molecules. $Sc_1(toluene)_2^-$ was identified as a sandwich complex anion in the gas phase. The electronic structures of the complex anions were observed by photoelectron spectroscopy.

Since the discovery of ferrocene,[1] $(C_5H_5)Fe(C_5H_5)$, organometallic sandwich compounds have attracted a lot of interest, and have been investigated considerably both experimentally and theoretically to figure out metal–molecule interactions.[2] The stability of the complexes is qualitatively explained by counting a number of valence electrons. Since it is deduced that the 18 electrons occupy all its valence orbitals, namely, five d, one s, and three p orbitals as fully as possible in metal-ligand bonding, organometallic complexes having 18 valence electrons are expected to be very stable.

Bis(benzene)vanadium (V_1Bz_2) has 17 valence electrons in total, where there are 5 electrons for one vanadium atom and 6 electrons each for two benzene molecules. According to the 18-electron rule, it was anticipated that V_1Bz_2 should be stabilized by an electron attachment. However, it was experimentally concluded that V_1Bz_2 has negative electron affinity (EA) on the contrary to the 18-electron rule.[3]

In the present study, we could successfully produce an anion of a full sandwich complex in the gas phase as bis(toluene)scandium anion having 16 valence electrons. A photoelectron spectroscopy (PES) on scandium complex anions has been performed to reveal the character of their molecular orbitals.

Details of experimental setup have been provided elsewhere.[4] Here only a brief description is given. Organometallic complex anions were prepared through the reaction between laser vaporized metal atoms and arene molecules. Scandium (Sc) metal atoms were vaporized by the irradiation of the second harmonic of a pulsed Nd^{3+}:YAG laser (532 nm), and the resulting plasma was cooled by a pulsed He carrier gas. Then the Sc atoms were sent into a flow-tube reactor where benzene (Bz) or toluene (Tol) vapor seeded in He was injected.

The produced complex anions were accelerated by applying a pulsed electric field (1–3 keV) to analyze by time-of-flight (TOF) mass spectrometer. In the case of measurement of PES spectra, the accelerated complex anions were mass-selectively decelerated by a potential elevator. The selected anions were photodetached with the third harmonic wavelength of another Nd^{3+}:YAG laser (355 nm; 3.49 eV). The kinetic energy of the ejected photoelectrons was analyzed by their TOF with a magnetic bottle spectrometer.

Figure 1 shows a TOF mass spectrum of Sc-Tol complex anions produced by the reaction of laser vaporized scandium atoms with toluene vapor. A series of the complex anions containing one toluene molecule, as indicated by (n,m) = (1,1), (2,1), (3,1), and (4,1), was observed similarly as the mass spectra of transition metal and benzene or toluene.[3] For (n,1), they are presumed to be an n atom cluster coated by a toluene molecule. In addition, it should be emphasized that $Sc_1Tol_2^-$;(1,2) was also observed. This is the first observation of the full sandwich complex anion in the gas phase.

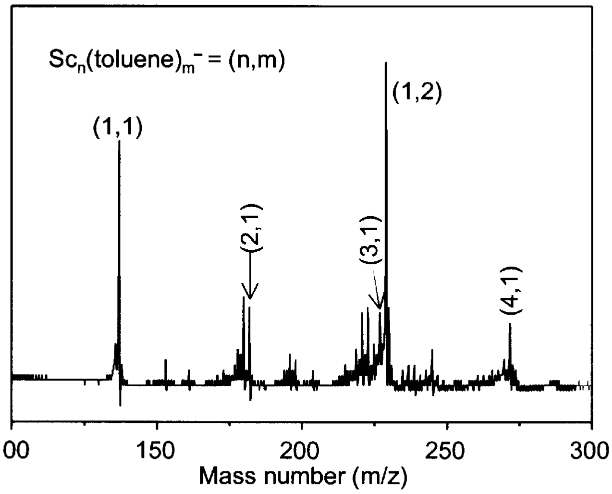

Figure 1. TOF mass spectrum of scandium-toluene complex anions. The peaks are labeled according to the notation (n,m), denoting the number of scandium atoms (n) and toluene molecules (m). Some of the peaks accompany those of dehydrogenated species.

As reported in our previous work,[3] the generation of full sandwich complex anions of $V_1Bz_2^-$ is impossible irrespective of the satisfaction of the 18-electron rule. This reason is rationalized by a molecular orbital model. Metal 3d orbitals split into three levels with benzene ligand. The $3d_{xz}$ and $3d_{yz}$ orbitals (e_{1g}) interact with benzene π orbitals, forming anti-bonding orbitals. The $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals (e_{2g}) interact with the benzene π^* orbitals, forming bonding orbitals. The $3d_{z^2}$ orbital (a_{1g}) cannot interact benzene orbitals and remains a non-bonding orbital. Since vanadium atoms have 5 valence electrons, they occupy two bonding orbitals (e_{2g}) and one non-bonding orbital (a_{1g}) with half-fill. To produce the $V_1Bz_2^-$ anion, one more electron should occupy the half-filled non-bonding orbital, and completes a closed shell. However, the excess electron occupying the non-bonding orbital (a_{1g}) is repelled by the benzene π electrons, and therefore V_1Bz_2 has negative EA. For Sc^- atom anion, the number of its valence electrons is 4, and it is possible that all valence electrons occupy the bonding orbitals (e_{2g}). The occupation of excess electron to the bonding orbitals made it possible to produce the full sandwich complex anion, $\mathrm{Sc_1Tol_2}^-$. Since the benzene complexes have one non-bonding orbital (a_{1g}), the system having 16 valence electrons should complete all the bonding orbitals without filling electrons into the a_{1g} orbital, which is satisfied only in Sc-benzene derivative complex anions.

A PES study was carried out to reveal the electronic structures of scandium complex anions. Figure 2 shows PES spectra of the half sandwich complex anions, $\mathrm{Sc_1Bz_1}^-$, and $\mathrm{Sc_1Tol_1}^-$. The first peak (X) in Figure 2 exhibited a sharp feature in both the spectra. In the photodetachment process, the Franck–Condon factor depends on the spatial overlap of the vibrational wave functions between the anion and the neutral. The degrees of freedom of a bending or a rocking vibration having low frequency should be inevitably accompanied with the change of the structures, and the peaks of these excited vibrations cannot be observed separately due to lacking of spectral resolution. Then, a large geometrical change generally gives a broad feature. The sharp peaks in Figure 2 mean that the geometry of the anion and the neutral are almost the same. According to the molecular orbital model, the less geometric change between the anion and the neutral can be explicable by the photodetachment of a non-bonding orbital. The excess electron should occupy the non-bonding orbital (a_1) localized on metal $3d_{z^2}$ or 4s orbital, and the first peak in the spectra was derived from this detachment. The second (A) and the third (B) peaks provide information of other orbitals although a theoretical calculation is necessary for their assignments.

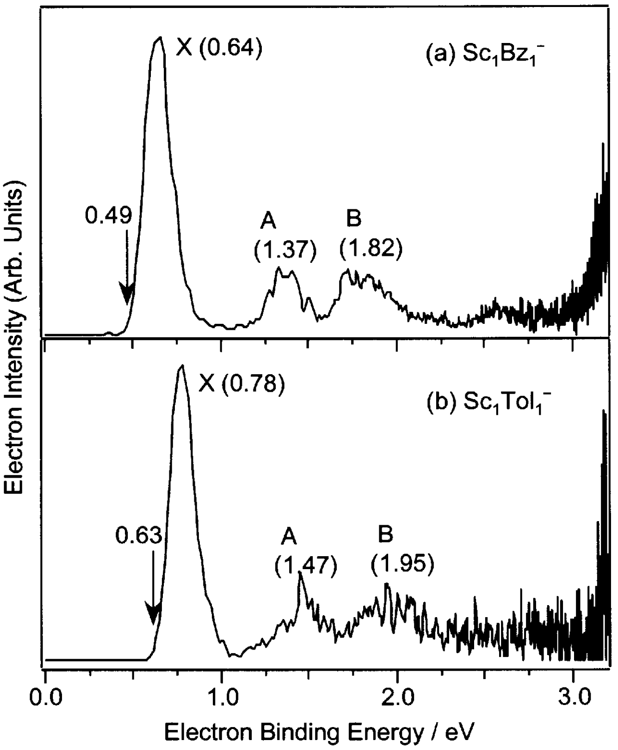

Figure 2. PES spectra of (a) $\mathrm{Sc_1Bz_1}^-$, and (b) $\mathrm{Sc_1Tol_1}^-$. The horizontal axis corresponds to the electron binding energy, defined as $E_b = h\nu - E_k$, where E_k is the kinetic energy of photoelectrons. Arrows indicate threshold energy (E_T), and E_T corresponds to the upper limit of the adiabatic electron affinity (EA).

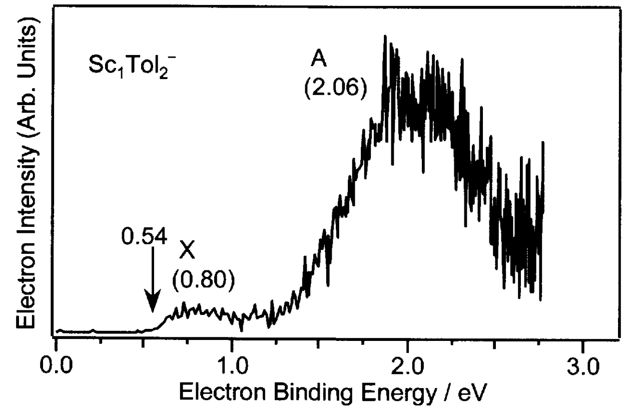

Figure 3. PES spectrum of $\mathrm{Sc_1Tol_2}^-$. Arrow indicates threshold energy (E_T), and E_T corresponds to the upper limit of the adiabatic electron affinity (EA).

Figure 3 shows a PES spectrum of the full sandwich complex anion, $\mathrm{Sc_1Tol_2}^-$. The broad features were observed in contrast with the PES spectra of $\mathrm{Sc_1Bz_1}^-$ and $\mathrm{Sc_1Tol_1}^-$. The broad peak (X) manifests that the excess electron of $\mathrm{Sc_1Tol_2}^-$ occupied the bonding orbital (e_{2g}). The occupation of bonding orbitals of excess electron on the full sandwich complex anions, $\mathrm{Sc_1Tol_2}^-$, was identified by the PES spectrum. The second peak (A) might correspond to the detachment of the benzene π orbitals that also have the nature of bonding orbitals.

Although all valence electrons of $\mathrm{Sc_1Bz_2}^-$ can occupy the bonding orbitals in the same way to $\mathrm{Sc_1Tol_2}^-$, the anion of $\mathrm{Sc_1Bz_2}^-$ has not been produced yet. Two explanations are considerable;(1) extremely low or negative EA and (2) low formation rate. As found in comparison with the PES spectra of $\mathrm{Sc_1Bz_1}^-$ and $\mathrm{Sc_1Tol_1}^-$ (see Figure 2), methyl substituent gives larger EA, which means that the complexes can be stabilized more by receiving an electron. Furthermore, it has been revealed that the toluene molecule can be reacted to the neutral transition metal atom more efficiently than benzene.[5] Indeed, the abundance of toluene complexes was larger than benzene in the mass spectra. In conclusion, both the factors of methyl substituent of benzene and the occupation of excess electron to bonding orbitals enabled us to form of the full sandwich complex anion, $\mathrm{Sc_1Tol_2}^-$.

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Reference and Notes

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