

# Mass Spectrometric Studies on Metal-hexafluorobenzene Anionic Complexes(M=Ag, Au, Pd, Pt, Pb and Bi)

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**Abstract** The anionic products from the reactions between metal(M=Ag, Au, Pd, Pt, Pb and Bi) vapour produced by laser ablation and hexafluorobenzene seeded in carrier gas(Ar) were studied by means of a homemade reflectron time-of-flight mass spectrometry(RTOF-MS). Experimental results show that the dominant products were  $[M_mC_6F_6]^-$  complexes for the reactions of Ag, Au, Pd and Pt with  $C_6F_6$ , while the dominant products were  $[M_mC_6F_5]^-$  complexes for the reactions of Pb and Bi with  $C_6F_6$ . The formation mechanisms of the products, including the adsorption of metal cluster anions on hexafluorobenzene and the C—F cleavage induced by metal cluster anions, were discussed.

**Keywords** Time-of-flight mass spectrometer; Metal cluster; Anionic complex; Reaction mechanism

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## 1 Introduction

The interactions of metals with organic molecules are of fundamental interest to chemical and material sciences. Compounds consisting of metal clusters and multiple organic molecules are prevalent in classical organometallic and coordination chemistry, which could provide useful information for further understanding some important heterogeneous catalytic processes<sup>[1—4]</sup>.

In recent years, many experimental<sup>[5—16]</sup> and theoretical<sup>[17—20]</sup> investigations on the interactions of metal clusters with benzene in gas phase have been reported. Armentrout *et al.*<sup>[12,13]</sup> studied  $MBz_2^+$  (M=Ti—Cu, Ag; Bz=benzene) *via* collision-induced dissociation experiments. Duncan group<sup>[9,14]</sup> conducted photodissociation studies on  $MBz^+$  (M=Fe, Mg, Ag and Bi) and  $VBz^+$  by means of infrared absorption spectroscopy. Bowers *et al.*<sup>[10]</sup> investigated vanadium/benzene cationic clusters by ion mobility spectrometry. Lin *et al.*<sup>[11]</sup> studied the dissociation of  $M_nBz^+$  and  $CrBz^+$  by Fourier transform-ion cyclotron resonance(FT-ICR). Nakajima and Kaya<sup>[5—7,16]</sup> performed mass spectrometry and photoionization studies on M-Bz clusters and their cations(M=Sc—Cu) as well as the studies of vanadium-arena anionic complexes by photoelectron spectroscopy(PES). Eber-

hardt<sup>[21]</sup> carried out PES studies of  $M_2Bz^-$  (M=Pt, Pd, and Pb) cluster anions. Bowen group<sup>[22—24]</sup> conducted PES studies of  $M_m(Bz)_n^-$  (M= Ti, Co, Fe, Ni) cluster anions. It is known that benzene molecules are prone to being dissociated by metal anionic clusters. On the surface of many active metal clusters, for example V<sup>[25]</sup>, Pt<sup>[26]</sup>, Nb and Rh<sup>[27]</sup>, benzene can be dehydrogenated or dissociated, wherein the hydrogen atoms are always observed to evolve as H<sub>2</sub> since the reactions are thermodynamically preferred. Besides, the study on the interaction of transition metal and phenyl was reported. Xing *et al.*<sup>[28]</sup> reported the generation of  $[M_m\text{phenyl}]^-$  (M=Mn, Cu) complexes. The phenyl-coinage metal complexes  $[Ag_mC_6H_5]^-$  and  $[Au_mC_6H_5]^-$  ( $m=1—3$ ), and the phenyl-lead metal complexes  $[Pb_mC_6H_5]^-$  ( $m=1—5$ ) were studied by virtue of PES and density functional theory(DFT)<sup>[29,30]</sup>.

For hexafluorobenzene, the substitution of fluorine for hydrogen on the benzene ring can bring the change of the bond strength of ionic  $\pi$  complexes. The substitution of fluorine for hydrogen on the benzene ring should set stronger anionic binding with benzene-ring fluorination, but this fact has apparently not been verified experimentally. The study of the reactions of metals with  $C_6F_6$ <sup>[31—33]</sup> has not been extended. Kaya group<sup>[31]</sup> studied  $[(C_6F_6)_n]^-$  and  $[Au(C_6F_6)]^-$

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complexes by PES. Dunbar *et al.*<sup>[32]</sup> studied the reactions of  $\text{Au}^+$  and  $\text{Au}^-$  with  $\text{C}_6\text{F}_6$ . However, little is known about the possibilities for anions attached to  $\pi$  face of benzene. The clustering of fluoride<sup>[34]</sup> and chloride<sup>[35,36]</sup> ions with some aromatics, including some partially fluorinated benzenes, has been reported, and it is considered that these are hydrogen-bound complexes not to be very relevant to the  $\pi$ -bound complexes of metal anions.

We carried out a mass spectrometric investigation of the reactions between hexafluorobenzene seeded in carrier gas and metal ( $M=\text{Ag, Au, Pd, Pt, Pb}$  and  $\text{Bi}$ ) vapour produced by laser ablation. Electronically, Ag and Au have a filled  $d^{10}$  shell combined with a  $5s^1$  and  $6s^1$  valence shell, respectively. Pd and Pt have a  $4d^{10}$  and  $5d^9 6s^1$  valence shell, respectively. And Pb and Bi have a  $6s^2 6p^2$  and  $6s^2 6p^3$  valence shell, respectively. Because of their different valence electrons, the dominant products of the reactions of these metals with  $\text{C}_6\text{F}_6$  are different from each other. The reaction mechanisms, including the adsorption of metal cluster anions on hexafluorobenzene and the selective C—F cleavage of the hexafluorobenzene induced by metal cluster anions were proposed.

## 2 Experimental Methods

The apparatus used in the experiments mainly consisted of a homemade reflectron time-of-flight mass spectrometer (RTOF-MS) with a laser system. The detail of the apparatus has been published elsewhere<sup>[37]</sup>, and only an outline is given below.

The metal ( $M$ ) disk targets (purity > 99.9%) in the source chamber of RTOF-MS were ablated by a pulsed laser beam (1064 nm or 532 nm Nd:YAG laser, 5 Hz, ~10 mJ/pulse) and the targets were rotated during the experiments. The laser-induced plasma was carried by the molecular beam generated from a pulsed valve at a backing pressure of about 400 kPa of argon (purity 99.99%), in which hexafluorobenzene was seeded. The volume ratio of hexafluorobenzene in the mixed gas was not more than 0.1%. The  $M_m$ -hexafluorobenzene anions generated from the reactions of metals with hexafluorobenzene were entrained by the carrier gas that underwent a low pressure ( $10^{-2}$  Pa) in the source chamber. After passing a skimmer, all the products entered into the acceleration area in the spectroscopic chamber ( $10^{-4}$  Pa). The anionic clusters were accelerated in the direction perpen-

dicular to the molecular beam and were reflected toward the detector, microchannel plates (MPC). The resolution ( $M/\Delta M$ ) of RTOF-MS is better than 2000, so it is easy to assign the products by the mass spectrum.

## 3 Results and Discussion

The anionic products from the reactions of all the studied metal samples with  $\text{C}_6\text{F}_6$  were generated under the similar experimental conditions as shown above. The wavelength of the laser (1064 nm or 532 nm) used for the ablation had little effect on the product distribution. The seeding of hexafluorobenzene in the carrier gas (Ar) can promote the growth of metal clusters whose underlying mechanism has been reported in the published paper<sup>[28]</sup>. The reactions between metals and organic molecules can effectively relax the internal energy of the plasma generated by laser ablation on metal sample, which is advantageous to the formation of larger size cluster species in the starting part of the reaction channel. This phenomenon has already been observed in our previous experiments<sup>[28,38,39]</sup>.

The experiments show that the lower partial pressure of hexafluorobenzene (< 0.1% of the mixed gas) favors the formation of anionic clusters. Otherwise, some byproducts, such as multiple hexafluorobenzene complexes  $[(\text{C}_6\text{F}_6)_n]^-$ , would appear. The presentation of the dominant anionic products identified by the mass spectrum is not sensitive to the laser intensity and the pressure of carrier gas used in the experiments, which will be discussed in the following parts.

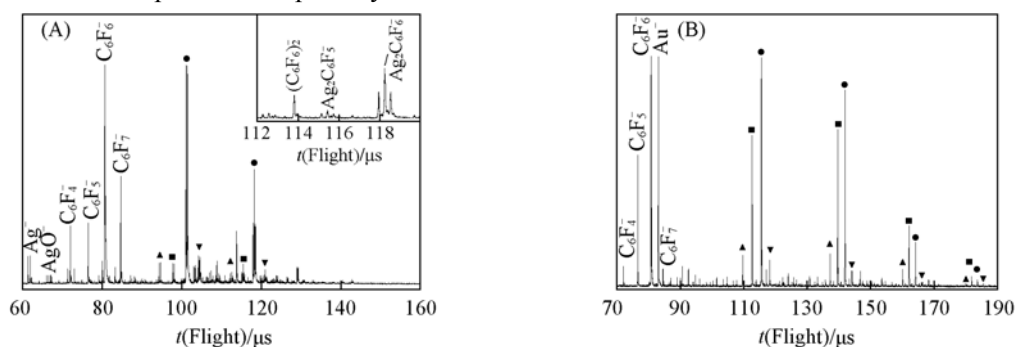
### 3.1 Product Analysis by Mass Spectrometry

Figs. 1—3 show the typical mass spectra of anionic products from the reactions between different vaporized metal species ( $M=\text{Ag, Au, Pd, Pt, Pb}$  and  $\text{Bi}$ ) and hexafluorobenzene molecules, respectively. The high resolution of RTOF-MS allows the exact identification of the isotopic distribution in the mass region of these spectra. All the mass spectra were carefully calibrated according to the mass number of pure metal clusters.

Figs. 1(A) and (B) show the anionic products from the reactions of Ag with hexafluorobenzene and Au with hexafluorobenzene. From Fig. 1, we can identify four different series of anionic complexes:  $[\text{M}_m\text{C}_6\text{F}_4]^-$ ,  $[\text{M}_m\text{C}_6\text{F}_5]^-$ ,  $[\text{M}_m\text{C}_6\text{F}_6]^-$  and  $[\text{M}_m\text{C}_6\text{F}_7]^-$  ( $M=\text{Ag}$  and  $\text{Au}$ ), and  $[\text{M}_m\text{C}_6\text{F}_6]^-$  complexes are do-

minant anionic products. The intensities of these complexes in mass spectrum decrease with the increase of number  $m$ . These results are in agreement with the published results<sup>[31,32]</sup>. The difference between the complexes containing Ag or Au is that the number  $m$  of Ag can reach 2 and the number  $m$  of Au can reach 4. However, for the reactions of Ag and Au with benzene, the dominant products are  $[M_mC_6H_5]^-$  ( $M=Ag$  and  $Au$ ,  $m=1-3$ ) dehydrogenated complexes<sup>[29]</sup>, and there are no  $[M_mC_6H_4]^-$ ,  $[M_mC_6H_6]^-$  and  $[M_mC_6H_7]^-$  complexes according to the mass spectrum. Especially for the

reaction of Ag and benzene, many fragments  $[AgC_nH_k]^-$  ( $n=1-12$ ,  $k=1-5$ ) are presented based on the mass spectrum whose intensities are the same as the ones of the dominant products  $[Ag_mC_6H_5]^-$  ( $m=1, 2$ ). This fact shows that the benzene ring is broken up by Ag cluster anion. We can see that in Fig.1, the intensities of the peaks attributed to  $[Ag_2C_nF_k]^-$  ( $n=4-7$ ,  $k=4,5$ ) are very weak, which shows that the substitution of fluorine for hydrogen on the benzene ring favors the stabilization of the aromatic ring.

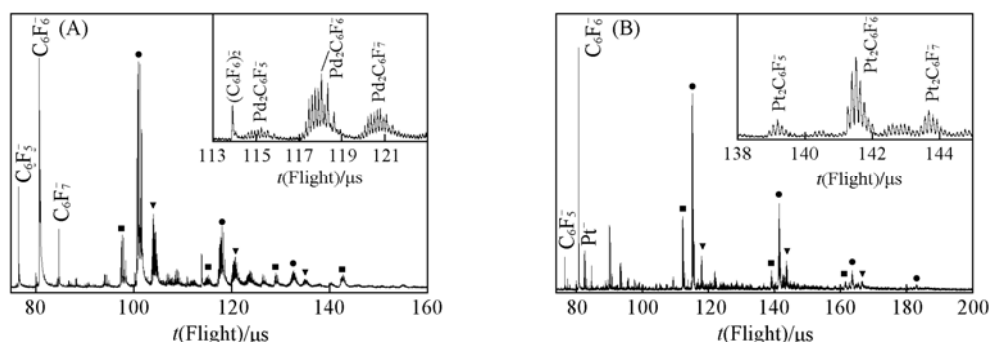


**Fig.1** Typical mass spectra of anionic products obtained from reactions between vaporized Ag(A), Au(B) and hexafluorobenzene, respectively

The inset in (A) shows the enlarged part of the spectrum. (A)  $\blacktriangle$   $Ag_mC_6F_4^-$  ( $m=1,2$ );  $\blacksquare$   $Ag_mC_6F_5^-$  ( $m=1,2$ );  $\bullet$   $Ag_mC_6F_6^-$  ( $m=1,2$ );  $\blacktriangledown$   $Ag_mC_6F_7^-$  ( $m=1,2$ ). (B)  $\blacktriangle$   $Au_mC_6F_4^-$  ( $m=1-4$ );  $\blacksquare$   $Au_mC_6F_5^-$  ( $m=1-4$ );  $\bullet$   $Au_mC_6F_6^-$  ( $m=1-4$ );  $\blacktriangledown$   $Au_mC_6F_7^-$  ( $m=1-4$ ).

Figs.2(A) and (B) show the anionic products from the reactions of Pd with hexafluorobenzene and Pt with hexafluorobenzene, respectively. In Fig.2, three series of  $[M_mC_6F_5]^-$  ( $m=1-3$ ),  $[M_mC_6F_6]^-$  ( $m=1-4$ ) and  $[M_mC_6F_7]^-$  ( $m=1-4$ ) ( $M=Pd$  and  $Pt$ ) complexes are identified, and the  $[M_mC_6F_6]^-$  complexes are dominant anionic products. The intensities of peaks assigned to these complexes in the mass spectra decrease with the increase of number  $m$ .

However, Liu *et al.*<sup>[40]</sup> reported that the products from the reaction between Pt and benzene are  $[Pt_mC_6H_4]^-$ ,  $[PtC_{12}H_k]^-$  and  $[Pt_mC_6H_4 \cdots (C_6H_6)_n]^-$  ( $m=1-4$ ) complexes and there are no  $[Pt_mC_6H_5]^-$ ,  $[Pt_mC_6H_6]^-$  and  $[Pt_mC_6H_7]^-$  complexes present. Eberhardt *et al.*<sup>[21]</sup> reported the chemisorption of benzene on Pd and Pt anions, but the resolution of their mass spectra was too poor to resolve the number of hydrogen atoms in the products.



**Fig.2** Typical mass spectra of anionic products obtained from reactions between vaporized Pd(A), Pt(B) and hexafluorobenzene, respectively

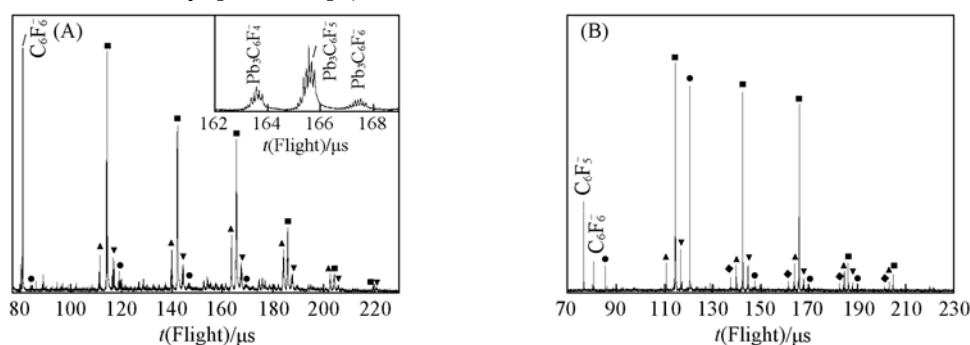
The insets in the spectra show the enlarged part of the spectra, respectively. (A)  $\blacksquare$   $Pd_mC_6F_5^-$  ( $m=1-3$ );  $\bullet$   $Pd_mC_6F_6^-$  ( $m=1-3$ );  $\blacktriangledown$   $Pd_mC_6F_7^-$  ( $m=1-4$ ). (B)  $\blacksquare$   $Pt_mC_6F_5^-$  ( $m=1-3$ );  $\bullet$   $Pt_mC_6F_6^-$  ( $m=1-4$ );  $\blacktriangledown$   $Pt_mC_6F_7^-$  ( $m=1-3$ ).

Figs.3(A) and (B) show typical mass spectra of the anionic products from the reactions of Pb with hexafluorobenzene and Bi with hexafluorobenzene. In Fig.3(A), the four series of  $[Pb_m]^-$ ,  $[Pb_mC_6F_4]^-$

( $m=1-5$ ),  $[Pb_mC_6F_5]^-$  and  $[Pb_mC_6F_6]^-$  ( $m=1-6$ ) are identified, and  $[Pb_mC_6F_5]^-$  defluorinated complexes are dominant anionic products. In Fig.3(B), the five series of  $[Bi_m]^-$  ( $m=1-5$ ),  $[Bi_mC_6F_3]^-$  ( $m=2-5$ ),

$[\text{Bi}_m\text{C}_6\text{F}_4]^- (m=1-5)$ ,  $[\text{Bi}_m\text{C}_6\text{F}_5]^- (m=1-5)$  and  $[\text{Bi}_m\text{C}_6\text{F}_6]^- (m=1-4)$  are identified, and  $[\text{Bi}_m\text{C}_6\text{F}_5]^-$  defluorinated complexes are dominant anionic products. These experimental results are similar to those of the reaction between Pb and benzene, in which the dominant products are  $[\text{Pb}_m\text{C}_6\text{H}_5]^- (m=1-5)$  dehydrogenated complexes<sup>[15]</sup>. Nevertheless, the difference is so prominent that for the reaction between Pb and  $\text{C}_6\text{H}_6$ , there are many  $[\text{Pb}_m\text{C}_n\text{H}_k]^- (m=1-2,$

$n=1-16, k=1-5)$  fragments and metal clusters  $[\text{Pb}_m]^- (m=1-11)$  present on the basis of the mass spectrum and they all have intense peaks. But for the reactions of Pb or Bi with  $\text{C}_6\text{F}_6$ , the intensities of  $[\text{M}_m\text{C}_n\text{F}_k]^- (m=1-4, n=4-6, k=1-3)$  fragments in the mass spectrum are very weak, which shows that the substitution of fluorine for hydrogen on the benzene ring favors the stabilization of the aromatic ring.



**Fig.3** Typical mass spectra of anionic products obtained from reactions between vaporized Pb(A), Bi(B) and hexafluorobenzene, respectively

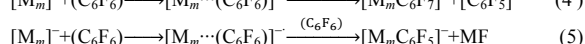
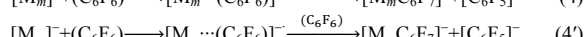
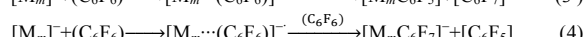
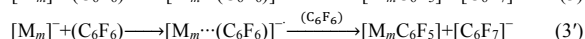
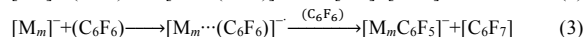
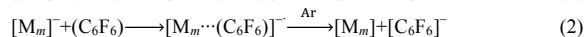
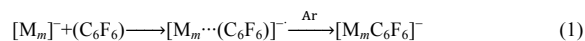
The inset in (A) shows the enlarged part of the spectrum. (A) ●  $\text{Pb}_m^- (m=1-6)$ ; ▲  $\text{Pb}_m\text{C}_6\text{F}_4^- (m=1-6)$ ; ■  $\text{Pb}_m\text{C}_6\text{F}_5^- (m=1-6)$ ; ▼  $\text{Pb}_m\text{C}_6\text{F}_6^- (m=1-6)$ . (B) ●  $\text{Bi}_m^- (m=1-5)$ ; ◆  $\text{Bi}_m\text{C}_6\text{F}_3^- (m=2-5)$ ; ▲  $\text{Bi}_m\text{C}_6\text{F}_4^- (m=1-5)$ ; ■  $\text{Bi}_m\text{C}_6\text{F}_5^- (m=1-5)$ ; ▼  $\text{Bi}_m\text{C}_6\text{F}_6^- (m=1-5)$ .

From the experimental results shown above, we can get the conclusion that the distributions of the products generated from the reactions between metals ( $\text{M}=\text{Ag}, \text{Au}, \text{Pd}, \text{Pt}, \text{Pb}$  and  $\text{Bi}$ ) and hexafluorobenzene are different from each other, and the dominant products from the reactions between metals ( $\text{M}=\text{Ag}, \text{Au}, \text{Pd}$  and  $\text{Pt}$ ) and hexafluorobenzene are different from those generated from the reactions between metals ( $\text{M}=\text{Pb}$  and  $\text{Bi}$ ) and hexafluorobenzene. Compared with the reactions of metals with benzene, the intensities of peaks of the  $[\text{M}_m\text{C}_n\text{F}_k]^-$  fragment products presented in the mass spectrum are very weak. This implies that the substitution of fluorine for hydrogen on the benzene ring favors the stabilization of the aromatic ring. It is known that the bond energy of phenyl—F is 54 kJ/mol higher than that of phenyl—H<sup>[41]</sup>. Some publications<sup>[42-45]</sup> show that the C—H bond activation reaction by transition metals is thermodynamically favorable and has less energy barrier than the C—F bond activation reaction. So if the metal cluster anions have not energy enough they can not destroy the aromatic ring of hexafluorobenzene.

### 3.2 Formation Mechanism

The formation mechanisms of the products  $[\text{M}_m\text{C}_6\text{H}_5]^-$  generated from the reactions of transition

metals or coinage metals with benzene have been discussed in previous publication<sup>[15,28,46]</sup>. Accordingly, the formation mechanisms of the anionic products  $[\text{M}_m\text{C}_6\text{F}_n]^- (m=1-6, n=5-7)$  are proposed as Scheme 1.



#### Scheme 1 Possible formation mechanisms of $[\text{M}_m\text{C}_6\text{F}_n]^- (m=1-6, n=5-7)$ complexes

From Figs.1—3, we can also see many anionic fragment products  $[\text{C}_6\text{F}_5]^-$ ,  $[\text{C}_6\text{F}_6]^-$  and  $[\text{C}_6\text{F}_7]^-$ . However, the experiments did not show that the cations  $[\text{C}_6\text{F}_5]^+$ ,  $[\text{C}_6\text{F}_6]^+$  and  $[\text{C}_6\text{F}_7]^+$  are totally observed in the same experiment. This fact implies that the generation of these anionic fragments results from the generation of metal anionic clusters. This situation is similar to that of the reactions between metals and benzene. Xing *et al.*<sup>[28]</sup> reported that the C—H cleavage of benzene was caused by the metal cluster anions.

For  $[\text{M}_m\text{C}_6\text{F}_6]^-$  products, the most possible mechanism is the pathway (1) in Scheme 1. In the cluster ion source, the metal species directly merge into

the hexafluorobenzene/argon reagent. The excess energy, which is left within metal clusters due to laser ablation or the collision process with hexafluorobenzene, can excite the reaction system to form  $[M_m \cdots (C_6H_6)]^-$  intermediate. And this intermediate is collided by Ar atoms subsequently, which takes away the excess energy to form  $[M_m C_6F_6]^-$  products, or breaks down the weak "bond" of the  $[M_m \cdots (C_6H_6)]^-$  intermediate to form  $[C_6F_6]^-$ , shown in the pathway (2) in Scheme 1.

For  $[M_m C_6F_5]^-$  and  $[M_m C_6F_7]^-$  products, the most possible mechanisms are the pathways (3) and (4) in Scheme 1. When the C—F bond is broken down due to the collisions between  $[M_m \cdots (C_6H_6)]^-$  and  $[C_6F_6]$ , the F atom can bond with  $[C_6F_6]$  to form  $[C_6F_7]$  and  $[M_m C_6F_5]^-$  complexes, or F atom bonds with  $[M_m C_6F_6]$  to form  $[M_m C_6F_7]^-$  and  $[C_6F_5]$ . The electron can also equally bond with  $[C_6F_5]$  and  $[C_6F_7]$ , so the pathway (3') and pathway (4') are both possible. The probability of the collision between  $[M_m \cdots (C_6H_6)]^-$  and  $[C_6F_6]$  is comparatively small due to the small volume ratio of  $[C_6F_6]$  in the carrier gas, so the intensities of the peaks of  $[M_m C_6F_5]^-$  and  $[M_m C_6F_7]^-$  in mass spectrum are weak. In order to pass through the above reaction pathways, it is needed to overcome the higher energy barrier of transition states(TS)<sup>[46]</sup> of the products. The excessive energy within hot metal clusters provided by laser vaporization is competent to overcome the energy barrier.

For heavy metals Pb and Bi, the dominant products are  $[M_m C_6F_5]^-$  complexes, and the  $[M_m C_6F_7]^-$  products disappear according to the mass spectrum. So the formation mechanism of  $[M_m C_6F_5]^-$  (M=Pb and Bi) is different from that of  $[M_m C_6F_5]^-$  (M=Ag, Au, Pd and Pt). The most possible formation mechanism of  $[M_m C_6F_5]^-$  is pathway (5) in Scheme 1. The heavy metals Pb and Bi ablated by laser are prone to form clusters  $[M_m]^-$ , which are identified in mass spectrum. When the intermediate  $[M_m \cdots (C_6H_6)]^-$  collides with metal M or  $[M_m]^-$ , an inset reaction with the cleavage of C—F bond takes place, and the product  $[M_m C_6F_5]^-$  yields with releasing F atom. The F atom can bond with M to form MF. This cleavage of C—F bond is not easy to take place due to the higher barrier of transition state(TS)<sup>[46]</sup>, and the excessive energy within hot metal clusters provided by laser vaporization promotes the formation of  $[M_m C_6F_5]^-$  complexes.

As for the bonding pattern of these dominant products, we propose the following bonding pattern. For the  $[M_m C_6F_6]^-$  complexes, the most possible bonding pattern is the interaction of metal clusters with  $\pi$ -orbital of  $C_6F_6$ <sup>[17,47,48]</sup>. For the  $[M_m C_6F_5]^-$  complexes, the most possible one is that the  $C_6F_5$  group bonds on the metal cluster *via* the metal-carbon  $\sigma$  bond<sup>[29,30,46]</sup>.

## 4 Conclusions

In summary, the reactions between the metal species(M=Ag, Au, Pd, Pt, Pb and Bi) vaporized by laser ablation and hexafluorobenzene seeded in carrier gas have been studied by a reflectron time-of-flight mass spectrometry. The anionic products gained from the reactions between metals and  $C_6F_6$  are metal-hexafluorobenzene complexes, which are different from the ones of the reactions between metals and benzene<sup>[28,29,40]</sup>. The dominant anionic products observed in Ag, Au, Pd and Pt systems are  $[M_m C_6F_6]^-$  complexes, and the ones observed in Pb and Bi systems are  $[M_m C_6F_5]^-$  defluorinated complexes. The reaction mechanisms of these products are proposed, including the adsorption of metal cluster anions on hexafluorobenzene and the C—F cleavage of hexafluorobenzene induced by metal clusters in the gas phase. To confirm the geometric structures of these complexes, the study by combination of the photoelectron spectroscopy and *ab initio* calculations for the  $[M_m C_6F_6]^-$  and  $[M_m C_6F_5]^-$  complexes is now underway.

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