Generation of $[M_m\text{-phenyl}]^-$ (M = Mn–Cu) complexes in the gas phase: Metal cluster anions inducement of a selective benzene C–H cleavage

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This article reports on the generation of $[M_m\text{-phenyl}]^-$ (M = Mn–Cu) complexes, which are very rare cases in chemistry. Experimental results showed that the typical cation products for the reactions of all 3d transition metal clusters (Sc–Cu) with benzene were different $[M_m(C_6H_6)_n]^+$ (M = Sc–Cu) species, while the typical anion products for the late 3d transition metals were $[M_m\text{–}C_6H_5]^-$ (M = Mn–Cu) complexes. Their formation mechanisms, which involve anion metal clusters inducing a selective benzene C–H cleavage in the gas phase, were proposed.

1. Introduction

Studies of the chemical interactions between metal clusters and organic molecules can provide useful information leading to deeper understanding of some important heterogeneous catalytic processes in the organometallic chemistry field.[1–3] The structures and properties of metal–aromatic molecular complexes have been studied extensively in recent years.[4–15] Duncan and coworkers[4–6] have investigated the formation and dissociation processes of metal–benzene complexes by reflectron time-of-flight mass spectrometry (RTOFMS) and laser photodissociation spectroscopy (LPDS). They have elucidated the dissociative charge-transfer processes of those complexes. Kaya and co-workers[7–9] have systematically studied the properties of 3d transition metal–benzene complexes ($[M_m(C_6H_6)_n]$ (M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni)) in the gas phase, including their structures, photodissociation processes, bonding energies, electron affinities, and ionization energies. They revealed two types of structures for those metal–benzene complexes: (i) multiple-decker sandwich structures; and (ii) metal clusters fully covered with benzene molecules (rice-ball structures). The sandwich structures are characteristic for the early transition metals (Sc–V), whereas the latter structures involve the late transition ones (Fe–Ni). Theoretical efforts in understanding their properties have recently been carried out by Pandey *et al.*[10] by using the density functional theory and generalized gradient approximation (DFT-GGA). All of their calculation results agreed well with the available experimental data. It should be noted that all these research efforts concerned only neutral or cation complexes. Very recently, several negative metal-cluster–benzene complexes were reported,[11–14] and their photoelectron spectra were studied.

On the other hand, the dissociation of benzene molecules on metal clusters is also an important topic because of the interest in the catalytic reaction intermediates. On the surface of many active metal clusters, for example V,[11] Pt,[15] Nb and Rh,[16] *etc.*, benzene can be dehydrogenated or dissociated, wherein the hydrogen atoms are always observed to evolve as H_2, since these reactions are thermodynamically preferred. In this article, we report on the generation of a rare kind of complexes, $[M_m\text{-phenyl}]^-$ (M = Mn–Cu), by the gas phase reaction of laser vaporized metal species with benzene vapor seeded in argon gas. The formation mechanisms, which involve metal cluster anions inducing the selective benzene C–H cleavage, were proposed.

2. Experimental

All product species were generated by the laser vaporization/inert carrier gas cooling the cluster ion source (shown in Fig. 1), and were analyzed using a home-made high resolution reflectron time-of-flight mass spectrometer (RTOFMS). Details of the mass spectrometry instrument are given elsewhere.[17] Briefly, the metal clusters were produced by laser ablation (1064 nm or 532 nm output of a pulsed Nd : YAG laser, about 10 mJ pulse^{-1}) on a target plate. The plate was rotated during the experiment process. The plume was carried downstream by the carrier gas (argon, typically 4 atm) from a pulsed valve (general valve, the typically open time was 300 μs), and confined in a channel that was 3 mm in diameter and 10 mm in length. The positively and negatively charged metal clusters in this channel were cooled to near-room temperature by the carrier gas and interacted with the benzene molecules seeded

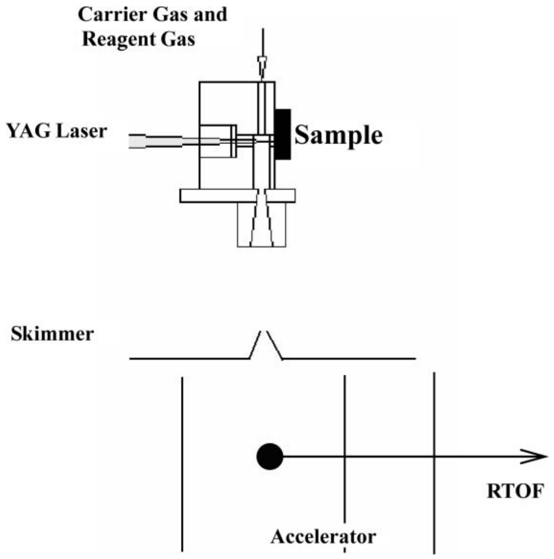

Fig. 1 Scheme of the laser vaporization/inert gas cooling cluster ion source.

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in argon simultaneously. All products expanded into a vacuum chamber with an operating pressure of *ca.* 10^{-4} Torr, then were skimmed into the accelerating area and analyzed by RTO-FMS. The timing sequence of the system (including valve opening, laser shoot, pulse acceleration and spectra recording) was controlled by a delay pulse generator (Stanford Research DG535). The best $M/\Delta M$ resolution that our mass spectrometer can reach is 2000, so we can easily resolve the number of the hydrogen atoms in the products.

The laser ablation targets were prepared by pressing pure metal powders into a tablet of 12 mm diameter and 5 mm thickness. Benzene (analytical reagent) was seeded in argon (purity 99.99%) in a vacuum stainless steel bottle (about 1 l) to yield a total pressure of 4 atm. The volume ratio of benzene in the mixed gas was no more than 2.5%. All materials and chemical reagents were obtained commercially with high purity and used as supplied without any further purification.

3. Results and discussion

Both positive and negative species were generated under similar experiment conditions for all studied systems. The wavelength of the ablating laser (1064 nm or 532 nm) had little effects on the product distribution. Seeding of benzene gas in the carrier gas (Ar) promoted the growth of metal clusters, since when only Ar was used the pure metal clusters were very small, and usually grew no large than M^+ or M_3^-. The underlying mechanism, we believe, involves the reactions with organic molecules effectively relaxing the internal energy of the laser ablation plasma, which was advantageous for the formation of larger size cluster species in the starting part of the reaction channel. We have observed similar phenomena in the reactions of lead clusters with alkene[18] and actone.[19]

In the negative product experiments where benzene were seeded, the lower partial pressure of benzene ($<0.5\%$ of the mixed gas) would be better. Otherwise, a large amount of byproducts, such as metal/carbon or metal/carbon/hydrogen cluster anions would appear. This was due to the complete dissociation and dehydration of benzene molecule in the laser ablated hot plasma, like in ref. 20. The dominant product species observed were not sensitive to the experimental conditions (laser intensity, the pressure of carrier gas, *etc.*) and they will be discussed in the following two parts.

A. Product analysis

Fig. 2 A–L shows the mass spectra of typical ion products in the reactions between vaporized metal species (Cr–Cu) and

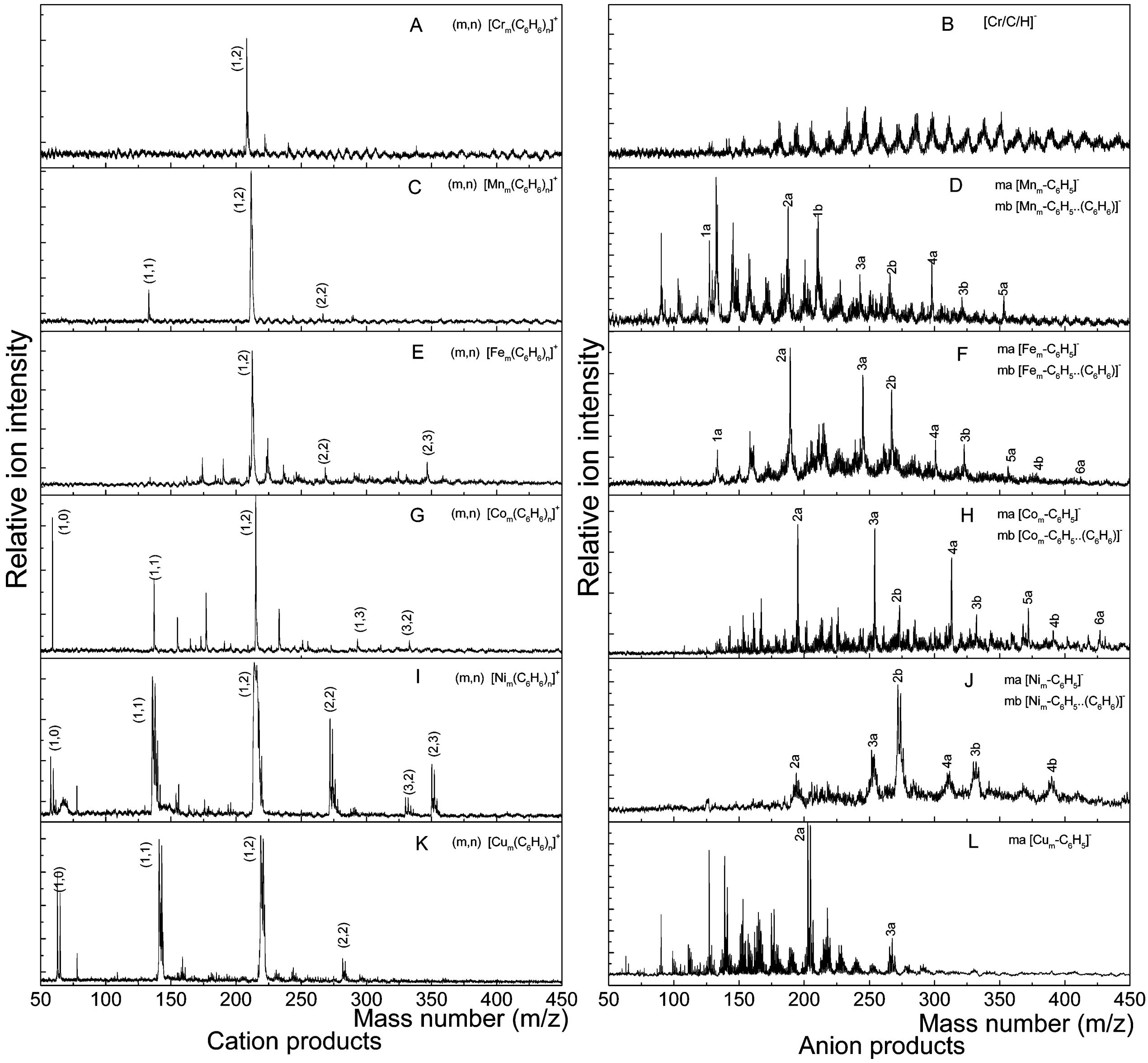

Fig. 2 Typical mass spectra of the ion products by laser vaporization/ionization of 3d transition metal samples (Cr–Cu) into a mixture of argon and benzene.

benzene molecules, respectively. The cation or anion products of Sc–V were similar with those of Cr and therefore not shown here. All the mass spectra were calibrated carefully according to the mass number of pure metal clusters. In some special cases (the peaks of pure metal clusters were absent), the I^- mass peak (resulting from trace amount of CH_3I mixed purposively in the carrier gas) in the spectrum was very helpful for mass calibration. As an example, we showed the enlarged part of mass spectra containing $[Co_m–C_6H_5]^-$ products and iodine anion mass peak in Fig. 3, which showed the hydrogen resolution.

Fig. 2 A, C, E, G, I and K shows the cation products for the reactions between Cr–Cu species and benzene respectively. $[M_m(C_6H_6)_n]^+$ (M = Sc–Cu) complexes were dominant cation products. These were in agreement with the previous results in many similar experiments.[4–9] The main anion products in the reactions between Sc–Cr species and benzene were various dehydrogenation speciess (metal/carbon/hydrogen species or even metal/carbon binary clusters). As an example, the anion products of Cr were shown in Fig. 2 B. In the reactions of late transition metal (Mn–Cu) anion species with benzene, $[M_m–C_6H_5]^-$ complexes were the main products. As shown in Fig. 2 D, F, H and J, $[Mn_m–C_6H_5]^-$ ($m = 1–5$), $[Fe_m–C_6H_5]^-$ ($m = 1–6$), $[Co_m–C_6H_5]^-$ ($m = 2–6$) and $[Ni_m–C_6H_5]^-$ ($m = 2–4$) complexes dominate their mass spectra respectively. For Cu metals, only smaller complexes were observed ($[Cu_m–C_6H_5]^-$ ($m = 1, 2$) shown in Fig. 2 L). Obviously, the most possible bonding pattern in these anion products is that the phenyl groups bond on the metal surfaces using the metal–carbon σ bond. These kinds of complexes, which contain a metal cluster-bound phenyl group are rare cases in chemistry. Until now, only a few examples $[M_3–C_6H_5$ (M = Ru, Pt, Ir, *etc.*) species with other ligands around (ref. 21 and therein)] have been reported. From the mass spectra, it was also found that $[M_m–C_6H_5]^-$ complexes containing Mn, Fe, Co and Ni metals could adsorb another benzene molecule, forming $[M_m–C_6H_5\cdots(C_6H_6)]^-$ species, in which two possible bond patterns (metal–carbon σ bond and metal surfaces/π-orbital of benzene interaction) exist. For example, $[Mn_m–C_6H_5\cdots(C_6H_6)]^-$ ($m = 1–3$), $[Fe_m–C_6H_5\cdots(C_6H_6)]^-$ ($m = 2–4$), $[Co_m–C_6H_5\cdots(C_6H_6)]^-$ ($m = 2–4$) and $[Ni_m–C_6H_5\cdots(C_6H_6)]^-$ ($m = 2–4$) complexes are clearly shown in Fig. 2 D, F, H and J.

B. Formation mechanisms

In the cation cases of these 3d transition metals, the formation of $[M_m(C_6H_6)_n]^+$ species was due to the strong interactions between the positive metal species and benzene molecules (including the attractive electrostatic interaction and the metal surfaces/π-orbital of benzene interaction). Their formation process involved the steps shown in eqns. (1) and (2).

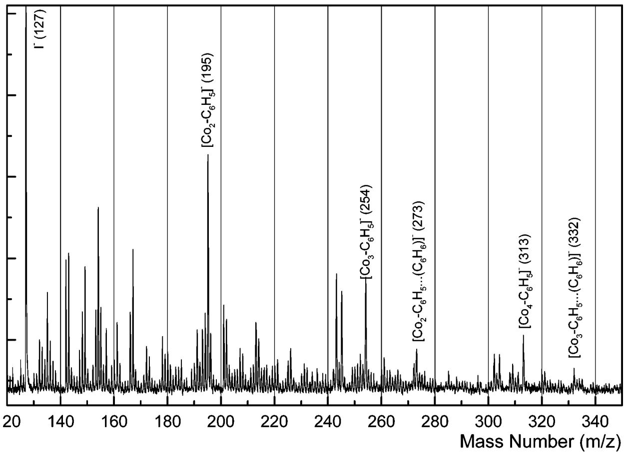

Fig. 3 Enlarged part of the mass spectrum containing anion Co/phenyl products and the iodine peak.

$$M_m^+ + (C_6H_6) \rightarrow [M_m(C_6H_6)]^{+*} \xrightarrow{Ar} [M_m(C_6H_6)]^+ \tag{1}$$

$$[M_m(C_6H_6)]^+ + n(C_6H_6) \rightarrow \left[M_m(C_6H_6)_{n+1}\right]^{+*} \xrightarrow{Ar} \left[M_m(C_6H_6)_{n+1}\right]^+ \tag{2}$$

In metal anion cases, repulsive electrostatic interaction existed between the electron-rich metal surfaces and the electron-rich benzene molecule. Niedner-Schatteburg *etc.*[16] studied the interaction of Nb_m^- and Rh_m^- with benzene under single-collision conditions. They found it is very reluctant to form metal cluster anions–benzene complexes unless the cluster contained up to tens of metal atoms. They attributed this to the effects of negative charge. The generation of metal cluster/phenyl complexes in this experiment has never been observed before. Their formation mechanism was proposed as eqns. (3) and (4). There are several reasons that support this anion reaction mechanism.

$$M_m^- + (C_6H_6) \rightarrow [M_m\cdots(C_6H_6)]^{-*} \rightarrow [M_m - C_6H_5]^- + [H] \tag{3}$$

$$[M_m(C_6H_5)]^- + (C_6H_6) \rightarrow [M_m - C_6H_5\ldots(C_6H_6)]^{-*} \xrightarrow{Ar} [M_m - C_6H_5\ldots(C_6H_6)]^- \tag{4}$$

(1) In all the mass spectra results, no free phenyl groups or ones adsorbed on metal cluster cations were observed. This implies that the C–H cleavage of benzene were caused by the metal cluster anions indeed.

(2) The selective C–H cleavage of benzene has been observed in many other cases. For example, on bulk metal surfaces electron induced dissociation (typically 10–50 eV) of adsorbed benzene can generate cleanly adsorbed phenyl groups. This is because the excitation of the C–H bond is faster than the quenching of formed $C_6H_6^+$ intermediates and therefore dynamically favored.[22,23] Electron–benzene (*ca.* 5–8 eV) interactions can also produce phenyl groups in the gas phase.[24] This process involves the repulsive states of benzene anions.

(3) In our cluster ion source, the metal species merged into the benzene/argon reagent directly. The excess energy (left within metal clusters due to laser vaporization or from the collision process with benzene) can excite the reaction system (forming $[M_m\cdots(C_6H_6)]^{-*}$), wherein the negative charges are partially transferred onto the benzene molecule. This can induce the C–H cleavage like the processes in electron–benzene interactions. Additionally, because the excited intermediates can be quenched quickly through the auto-detachment of an excess electron, the dissociation of metal and benzene parts or the collisions with argon, the faster C–H excitation process may be dynamically favored even though the H_2 elimination or C–C cleavage are thermodynamically preferred.

However, two questions still remain: (i) Why the benzene molecules were hardly adsorbed by the naked metal cluster anions while the produced $[M_m–C_6H_5]^-$ species can adsorb one more benzene molecule for Mn, Fe, Co and Ni? (ii) Why these metal cluster/phenyl complexes couldn't be observed on the early 3d transition metals (Sc–Cr)? As the analysis above show, it is in the repulsive electrostatic interaction between metal cations and benzene molecules that hardly any metal cluster/benzene complex anions were observed, though abundant cationic or neutral metal/benzene species can be generated under similar conditions.[7–9] When $[M_m–C_6H_5]^-$ was formed, the negative charge in the metal part could partially delocalize to the phenyl group through the metal–carbon bond, and therefore another benzene molecule could possibly be adsorbed on the metal parts. As for question (ii), the differences between neutral metal/benzene complexes of the late 3d transition metals and those of the early 3d transition metals have been well studied by Kaya *et al.*[9] They found that in the laser vaporized ion source, the late 3d metals (including Fe, Co, Ni, *etc.*) can form rice-ball structures, wherein benzene molecules cover on the surface of the metal part, while the early ones (Sc, Ti, V, *etc.*) form multiple sandwich structures, in which the metal atoms are separated by the benzene molecules. Bowers *et al.*[25] also found that even the originally generated V_n^+ clusters tend to reform to multiple sandwich structures in benzene vapor. This feature of the early 3d transition metals (tend to bond with metal atoms separately and sufficiently) can affect the properties of the intermediates $[M_m\cdots(C_6H_6)]^{-*}$ in eqn. (3) and the possible continuous reactions shown in eqn. (4). As a result, the dissociation process of benzene caused by the excess energy or the negative charge, was complicated.

In very recent research, Co/benzene complexes have been produced and studied using a similar cluster ion source.[14] The peak distribution of the mass spectra in the low benzene concentration case was very similar with our result shown in Fig. 2 H. However, the mass resolution in that experiment was not sufficient enough to distinguish whether an adsorbed phenyl fragment or adsorbed benzene molecule were formed on the metal part and we can't exclude the possibility that the products in that experiment were assigned incorrectly. Our results show conclusively that metal–phenyl complexes were formed in the experiment.

4. Conclusion

In summary, the reactions between laser vaporized 3d transition metal species and benzene vapors were studied. The cation products for all 3d metals (Sc–Cu) were metal/benzene complexes, which was in agreement with previous studies. However the typical anion products observed in Mn–Cu systems were $[M_m\text{–}C_6H_5]^-$ and $[M_m\text{–}C_6H_5\cdots C_6H_6]^-$ complexes. The reaction mechanisms were proposed, involving metal cluster anions inducement of selective benzene C–H cleavage in the gas phase.

Even though the adsorbed phenyl groups on metal surfaces are very rare cases in chemistry, they are important intermediates in many catalytic processes (such as Ullmann coupling reactions[26–28]). Verifying their structures and properties is essential for developing a microscopic level description of these important organic reactions. The detailed study on these complexes is now underway.

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References

1 Z. Xu, F. S. Xiao, S. K. Purnell, O. Alexeev, S. Kawi, S. E. Deutsch and B. C. Gates, *Nature (London)*, 1994, **372**, 346.
2 J. L. Whitten and H. Yang, *Surf. Sci. Rep.*, 1996, **24**, 59.
3 N. Toshima and T. Yonezawa, *New J. Chem.*, 1998, **22**, 1179.
4 K. F. Willy, P. Y. Chen, M. B. Bishop and M. A. Duncan, *J. Am. Chem. Soc.*, 1991, **113**, 4721.
5 K. F. Willy, C. S. Yeh, D. L. Robbins and M. A. Duncan, *J. Phys.Chem.*, 1992, **96**, 9106.
6 C. S. Yeh, K. F. Willy, D. L. Robbins and M. A. Duncan, *Int. J. Mass Spectrom. Ion Processes*, 1994, **131**, 307.
7 K. Hosshino, T. Kurikawa, H. Takeda, A. Nakajima and K. Kaya, *J. Phys. Chem.*, 1995, **99**, 3053.
8 T. Kurikawa, M. Hirano, H. Takeda, K. Yagi, K. Hoshino, A. Nakajima and K. Kaya, *J. Phys. Chem.*, 1995, **99**, 16248.
9 T. Kurkawa, H. Takeda, M. Hiranok, K. Judai, T. Arita, S. Nagao, A. Nakajima and K. Kaya, *Organometallics*, 1999, **18**, 1430.
10 R. Pandey, B. K. Rao, P. Jena and M. A. Blanco, *J. Am. Chem. Soc.*, 2001, **123**, 3799.
11 K. Judai, M. Hirano, H. Kawamata, S. Yabushita, A. Nakajima and K. Kaya, *Chem. Phys. Lett.*, 1997, **270**, 23.
12 G. Lüttgens, N. Pontius, C. Friedrich, R. Klingeler, P. S. Bechthokd, M. Neeb and W. Eberhardt, *J. Chem. Phys.*, 2001, **114**, 8414.
13 K. Judai, Y. Nakamura, M. Tachibana, Y. Negishi, A. Nakajima and K. Kaya, *Chem. Lett.*, 2001, 114.
14 M. Gerhards, O. C. Thomas, J. M. Nilles, W.-J. Zheng and K. H. Bowen, *J. Chem. Phys.*, 2002, **116**, 10247.
15 G. S. Jackson, F. M. White, C. L. Hammill, R. J. Clark and A. G. Marshall, *J. Am. Chem. Soc.*, 1997, **119**, 7567.
16 C. Berg, M. Beyer, U. Achatz, S. Joos, G. Niedner-Schatteburg and V. E. Bondybey, *J. Chem. Phys.*, 1998, **108**, 5398.
17 X. P. Xing, Z. X. Tian, P. Liu, Z. Gao, Q. H. Zhu and Z. C. Tang, *Chin. J. Chem. Phys.*, 2002, **15**, 83.
18 Z. X. Tian, X. P. Xing and Z. C. Tang, *Rapid Commun. Mass Spectrom.*, 2002, **16**, 1515.
19 Z. X. Tian, X. P. Xing and Z. C. Tang, *Rapid Commun. Mass Spectrom.*, 2003, **17**, 17.
20 Z. Y. Chen, G. J. Walder and A. W. Castleman, Jr., *Phys. Rev. B*, 1994, **49**, 2379.
21 M. I. Bruce, P. A. Humphrey, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1997, **539**, 141.
22 X. L. Zhou, M. E. Castro and J. M. White, *Surf. Sci.*, 1990, **238**, 215.
23 J. M. White, *Langmuir*, 1994, **10**, 3946.
24 J. G. Dillard, *Chem. Rev.*, 1973, **73**, 589.
25 P. Weis, P. R. Kemper and M. T. Bowers, *J. Phys. Chem. A*, 1997, **101**, 8207.
26 F. Ullmann and J. Bielecki, *Ber. Dtsch. Chem. Ges.*, 1901, **34**, 2174.
27 P. E. Fanta, *Chem. Rev.*, 1946, **38**, 139.
28 P. E. Fanta, *Chem. Rev.*, 1964, **64**, 61.