Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 136 (2015) 906–910

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

HRMS studies on the fragmentation pathways of metallapentalyne

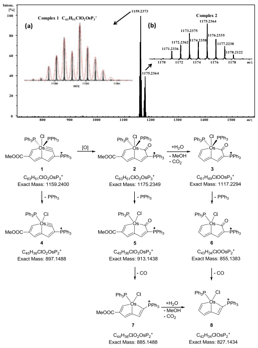
Zhiwei Lin *, Congqing Zhu, Haiping Xia

College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China

HIGHLIGHTS

- The ESI-FT-ICR MS using collision-induced dissociation (CID) method was applied to investigate the characteristic fragment ions of metalla-aromatic complexes for the first time.
- The fragmentation process of osmapentalyne, which contained metal-carbon triple bond in a five-membered ring, was discussed in detail.
- These characteristic fragmentation pathways were helpful to analyze and interpret the stability and property of the parent ion.
- This method could be used for the characterization of other organometallic complexes, especially containing characteristic isotopic peaks.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 May 2014
Received in revised form 22 September 2014
Accepted 25 September 2014
Available online 5 October 2014

Keywords:
Metallapentalyne
Osmium
Organometallic
ESI FT-ICR MS
HRMS
MS/MS

ABSTRACT

The electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) using collision-induced dissociation (CID) method was applied to investigate the characteristic fragment ions of metalla-aromatic complexes for the first time. The fragmentation process of osmapentalyne, which contained metal-carbon triple bond in a five-membered ring, was discussed in detail. The ESI FT-ICR MS CID experimental results at high resolution mass spectra (HRMS) demonstrated the elemental composition of fragment ions unambiguously, thus a reasonable fragmentation pathway of osmapentalyne was proposed. In addition, the characteristic fragment ions have been investigated, which were specific and useful for the identification of some osmapentalynes complexes. These characteristic fragmentation pathways were helpful to analyze and interpret the stability and property of the parent ion. Also, this method could be used for the characterization of other organometallic complexes, especially containing characteristic isotopic peaks.

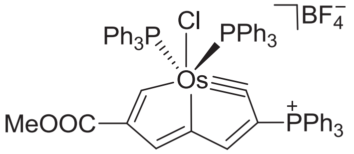
Introduction

Organometallics are highly useful in organic synthesis, homogenous catalysis, and material sciences. In most cases, single crystal X-ray diffractions are applied to elucidate the structure of organometallic compounds, which require that the sample must be well crystallized. However, it is sometimes difficult to obtain high-quality single crystals [1]. Alternatively, people use nuclear magnetic resonance (NMR) to obtain the structural information of the organometallic compounds, but this method cannot give

---

* Corresponding author.

http://dx.doi.org/10.1016/j.saa.2014.09.112



1-BF$_4$

Fig. 1. The structure of transition metal aromatic-osmium complex 1-BF$_4$.

accurate molecular weight and the fine structure, especially to those paramagnetic metal compounds [2]. In addition in some cases, elemental analysis (EA) are also used to characterize organometallics, whereas the results of EA are greatly influenced by environment, such as the temperature, humidity, the composition of air, and so on.

Mass spectrometry (MS) is a powerful tool in multi-disciplinary researches such as forensics, metabolomics, natural products, and food science [3–9]. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is uniquely advantageous over other mass analyzers because it provides higher resolving power and higher mass accuracy, and can isolate and observe ions for extended periods. Therefore FT-ICR MS is appropriate for the analysis of complex mixtures containing multiple ions of the same nominal mass, as well as for tandem mass spectrometry. When combined with ESI ionization source, FT-ICR MS can provide rapid, highly selective, and information-rich analysis [9–19].

Over the past decades, high resolution mass spectra (HRMS) has been widely utilized to analyze organometallics, however, rare attention has been paid upon their application in the fragmentation mechanism of organometallic compounds. Metalla-aromatics [20–24], a new branch of organometallic complexes, are receiving more and more attention due to their unique properties and potential applications. Although some metalla-aromatics have been reported over the past years [25–35], however, their structural characteristics and diversities are still limited because the access to high-quality crystals is much more difficult. Complementarily, HRMS studies on the fragmentation pathways of metalla-aromatics may facilitate the identification and elucidation of new metalla-aromatics.

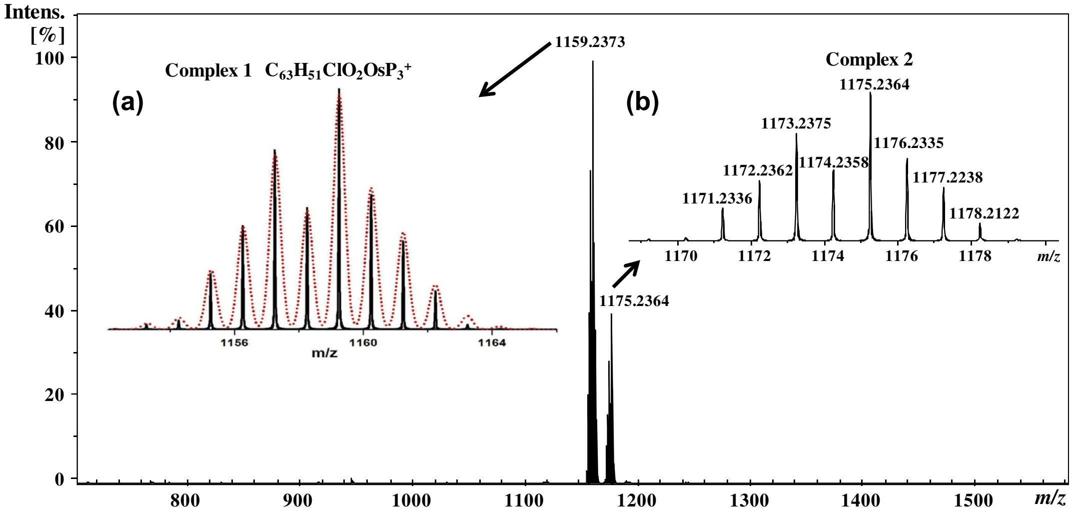


Fig. 2. (a) Mass spectrum of the $C_{63}H_{51}ClO_2OsP_3^+$. The measured (black trace) and simulated (red and dot trace) isotopic patterns of $C_{63}H_{51}ClO_2OsP_3^+$. (b) Mass spectrum of the $C_{63}H_{51}ClO_3OsP_3^+$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

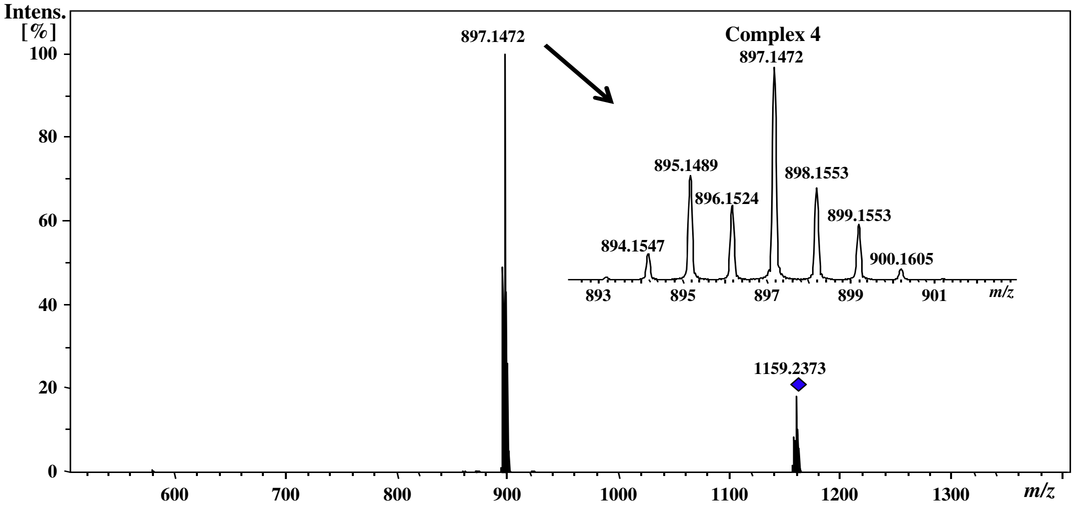
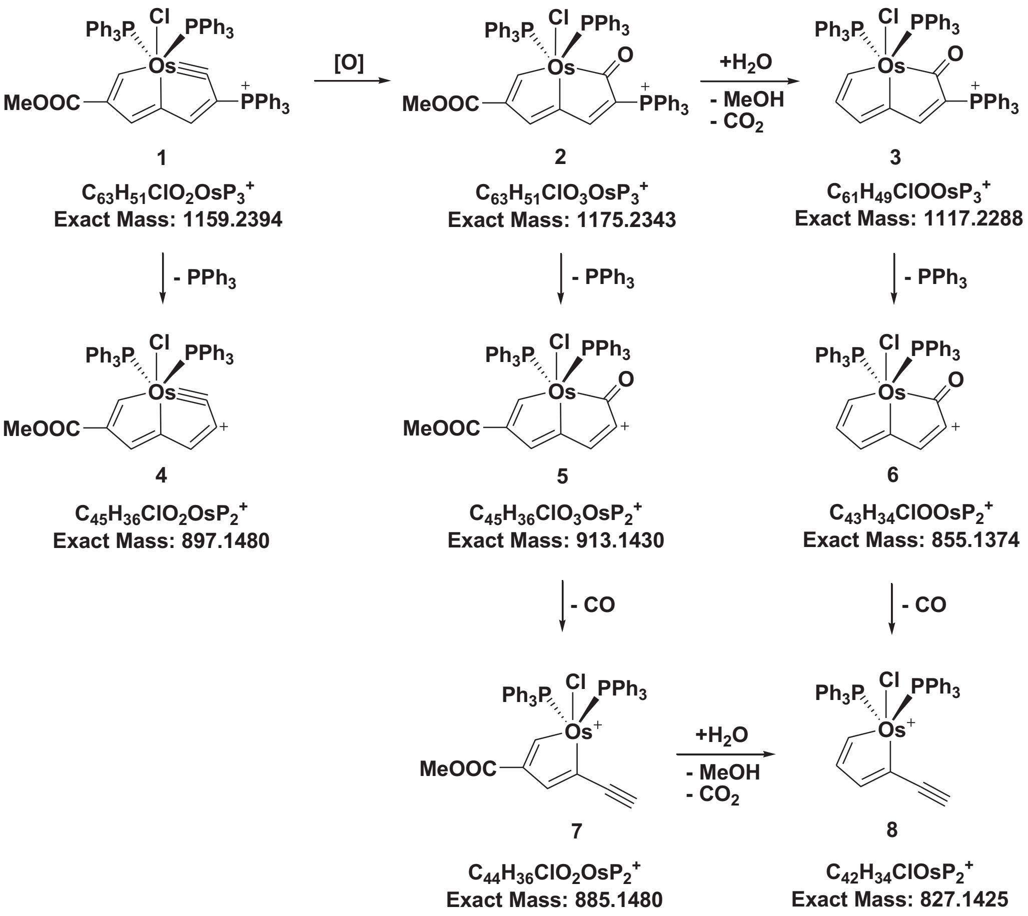


Fig. 3. The ESI FT-ICR MS CID fragmentation spectra of $C_{63}H_{51}ClO_2OsP_3^+$, m/z 1159.2373.

Table 1
Mass spectral data obtained in positive ion mode.

	Experimental mass (*m*/*z*, Da)	Theoretical mass (*m*/*z*, Da)	Error (ppm)	Formula of ion
Complex **1**	1159.2373	1159.2394	1.8	$C_{63}H_{51}ClO_2OsP_3^+$
Complex **2**	1175.2364	1175.2343	1.8	$C_{63}H_{51}ClO_3OsP_3^+$
Complex **3**	1117.2270	1117.2288	1.6	$C_{61}H_{49}ClOOsP_3^+$
Complex **4**	897.1472	897.1480	0.9	$C_{45}H_{36}ClO_2OsP_2^+$
Complex **5**	913.1418	913.1430	1.3	$C_{45}H_{36}ClO_3OsP_2^+$
Complex **7**	885.1481	885.1480	0.1	$C_{44}H_{36}ClO_2OsP_2^+$
Complex **6**	855.1370	855.1374	0.5	$C_{43}H_{34}ClOOsP_2^+$
Complex **8**	827.1422	827.1425	0.4	$C_{42}H_{34}ClOsP_2^+$



Scheme 1. Proposed fragmentation pathways by positive ESI MS/MS.

Osmapentalyne, a unique metalla-aromatic complex, exhibited excellent thermal stabilization although it contained a metal-carbon triple bond in a five-membered ring [36]. The structure of transition metal aromatic-osmium complex 1-BF4 was shown in Fig. 1. In the present study we reported its fragmentation pattern on ESI FT-ICR MS with the isotope distribution.

Experiments

MS spectrometry was obtained on Bruker Daltonics Apex ultra 7.0T Fourier transform mass spectrometer (Bruker Daltonics, Bremen, Germany) with an Electrospray ionization source (Apollo II, Bruker Daltonics, Bremen, Germany). The conditions employed for ESI source were a drying gas temperature of 180 °C, a nebulizing gas pressure of 2.0 L/min, with 4.0 kV on the atmospheric side of the glass capillary, 3.5 kV on the atmospheric chamber end cap shield, and the capillary exit voltage was kept 36 V to avoid capillary-skimmer dissociation in the ESI interface. All ion excitations were performed in broad band mode (frequency sweep radial ion excitation). Simulations of ion trajectories inside ICR cells in both thermal motion and also during radial excitation were well known and given in the literature [37]. The base pressure in the ICR vacuum chamber was 4.0 e−11 mbar and in the quadrupole region 6.0 e−6 mbar. High pressure in the quadrupole region was necessary to colinearize the ions in the radialplane and decelerate the radial components of the ion kinetic energy. CID experiments were also performed on specific product ions formed as a result of linear ion acceleration. For CID experiments, argon was used as the collision gas and the collision energy was set to 15 V.

Results and discussion

Positive electrospray ionization (ESI) often combines hydrogen ion during the spraying and evaporation process of the microdro-

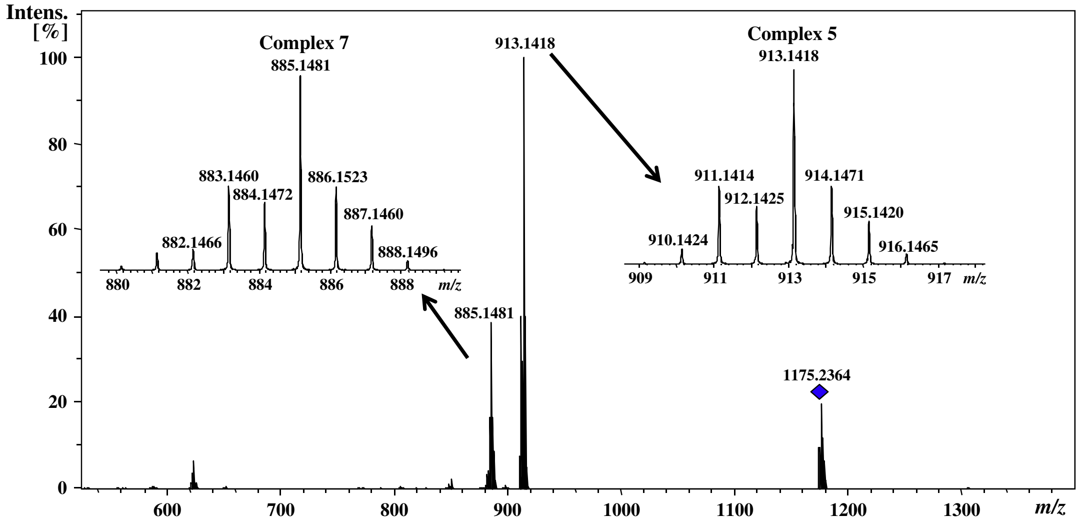


Fig. 4. The ESI FT-ICR MS CID fragmentation spectra of $C_{63}H_{51}ClO_3OsP_3^+$, m/z 1175.2364.

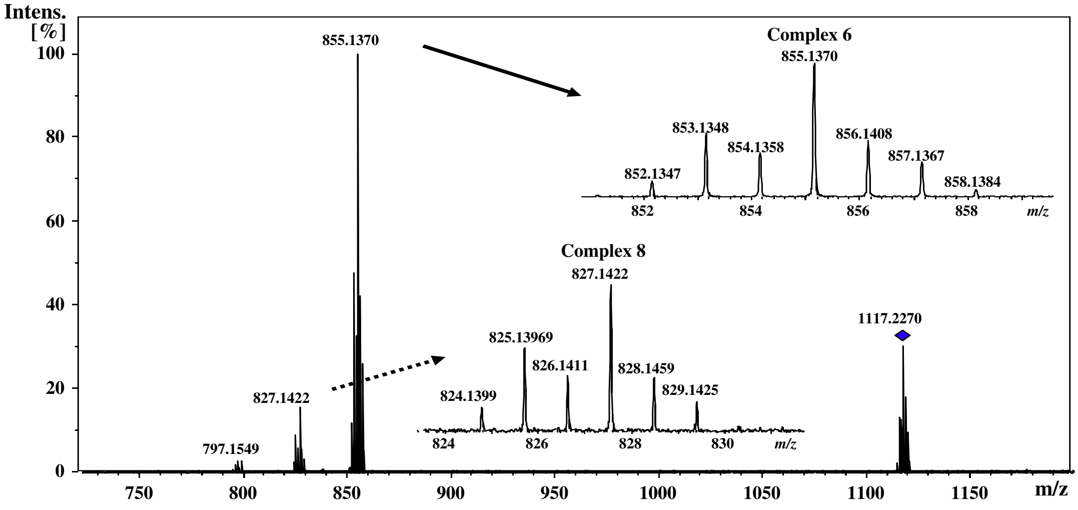


Fig. 5. The ESI FT-ICR MS CID fragmentation spectra of $C_{61}H_{49}ClOOsP_3^+$, m/z 1117.2270.

plets, which has been extensively studied since the early work initiated by Fenn et al [38]. But for the ionic compounds, generally only M^+ can be detected by the spectrometer in positive mode. The mass spectrum of $C_{63}H_{51}ClO_2OsP_3^+$ (complex **1**) was shown in Fig. 2. For complex **1**, the spectrum was quite clean, with a dominant molecular ion peak at m/z = 1159.2373, which is only 2.3 ppm difference from the theoretical value (1159.2394). The observed isotopic pattern of $C_{63}H_{51}ClO_2OsP_3^+$ was in good agreement with the simulated (Fig. 2a). A minor peak at m/z = 1175.2364 was observed, which was assigned as $C_{63}H_{51}ClO_3OsP_3^+$ (complex **2**) that was derived from the oxidation of $C_{63}H_{51}ClO_2OsP_2^+$ (Fig. 2b). An explanation for this was that the large ring strain in the five-membered ring of complex **1** made the metal-carbon triple bond easily be oxidized to form complex **2** under high temperature of the test conditions.

For MS/MS operation, product ion spectra were generated at 15 V collision energy. Fig. 3 showed the ESI FT-ICR MS CID fragmentation spectra of $C_{63}H_{51}ClO_2OsP_3^+$. Under the experimental conditions, complex **1** was prone to lose a triphenylphosphine (PPh_3) ligand in the osmium center into $C_{45}H_{36}ClO_2OsP_2^+$ (complex **4**). The molecular ion peak of complex **4** was observed at m/z = 897.1472, which was consistent with the theoretical value (m/z: 897.1472) accurately calculated from the Isotope Pattern software supplied by Bruker company. Isotope Pattern software could afford us much important information about the fragmentation ions, for example, one major peak with m/z 913.1418 (complex **5**) appeared in the MS/MS spectra, which was 262.0946 Da less than the quasi-molecular ion peak. The corresponding elemental composition of the neutral fragment was assigned as PPh_3. The other peaks were calculated by the same method. The formulae of main potential ionic fragments were listed in Table 1. The mechanism of proposed fragmentation pathways was shown in Scheme 1.

However, complex **1**, $C_{63}H_{51}ClO_2OsP_3^+$ (m/z 1159.2373) was easily oxidized to complex **2**, $C_{63}H_{51}ClO_3OsP_3^+$ (m/z 1175.2364), then there were two cleavage pathways. In the first cleavage pathway which could been clearly seen in Fig. 4, one of the PPh_3 ligands in the osmium center was lost, which formed $C_{45}H_{36}ClO_3OsP_2^+$ (complex **5**)with a m/z 913.1418. Then the carbonyl group was lost under high temperature, leading to the formation of $C_{44}H_{36}ClO_2OsP_2^+$ (complex **7**) with molecular ion peak at m/z = 885.1481. Interestingly, the $-COOCH_3$ group in complex **7** was hydrolyzed into $-COOH$ by the trace water of methanol, and then decarboxylated in high temperature up to 180 °C, leading to a new molecular ion peak at m/z = 827.1422 ($C_{42}H_{34}ClOsP_2^+$, complex **8**). Another cleavage pathway which could be obtained in Fig. 5 was to form complex **3**, $C_{61}H_{49}ClOOsP_3^+$. It should be noted that complex **3** (*m*/*z* 1117.2270) in the primary mass could not be clearly seen, but when the isolation window was set to 1117.2 Da, it was still a strong peak. The likely reason was that $-COOCH_3$ group in complex **2** was hydrolyzed into –COOH, and then lost one of CO_2 under high temperature, which was similar to the formation of complex **8** from complex **7**. With the slow increase of collision energy in MS/MS, two major strong peaks with *m*/*z* 855.1370 (complex **6**) and *m*/*z* 827.1422 (complex **8**) were found. A reasonable explanation for this observation was that complex **3** first lost one of the PPh_3 ligands in the osmium center, leading to the formation of $C_{43}H_{34}ClOOsP_2^+$ (complex **6**) with a *m*/*z* 855.1370. However, the carbonyl group in the five-membered ring of complex **6** was prone to dissociation, which resulted in the formation of a four-membered ring complex **8** via ring contraction reaction.

Finally, the ESI-MS/MS mass spectra of compound **1** and its fragment ions were summarized in Table 1. It was clear that each error between the measured and the theoretical value was less than 2.5 ppm, which was accurate for structural elucidation studies.

Conclusion

The logical fragmentation pathways of the compound in positive mode have been proposed by ESI FT-ICR MS, which is important for the rapid identification of organometallic compounds. The molecular weight and the characteristic fragment ions obtained by MS/MS are consistent with the basic molecular structure. In combination with the isotope distribution, ESI FT-ICR MS plays a significant role in the identification of metal compounds and fragmentation mechanism. This study has extended the application scope of HRMS and offered a new way for the investigation of reaction mechanism of organometallics. Further studies aimed to exploit the fragmentation pathways of other organometallic complexes are in progress.

Acknowledgement

This work was supported by the 973 Program (2012CB821600) and the National Science Foundation of China (Nos. 21332002).

References

[1] G.X. Jin, Coord. Chem. Rev. 248 (2004) 587–602.
[2] G.R. Fulmer, A.J.M. Miller, N.H. Sherden, H.E. Gottlieb, A. Nudelman, B.M. Stoltz, J.E. Bercaw, K.L. Goldberg, Organometallics 29 (2010) 2176–2179.
[3] R.R. Steiner, R.L. Larson, J. Forensic Sci. 54 (2009) 617–622.
[4] Z. Takáts, J.M. Wiseman, R.G. Cooks, J. Mass Spectrom. 40 (2005) 1261–1275.
[5] O.P. Haefliger, N. Jeckelmann, Rapid Commun. Mass Spectrom. 21 (2007) 1361–1366.
[6] N.E. Manicke, J.M. Wiseman, D.R. Ifa, R.G. Cooks, J. Am. Soc. Mass Spectrom. 19 (2008) 531–543.
[7] K.F. Blom, J. Am. Soc. Mass Spectrom. 9 (1998) 789–798.
[8] B. Zekavat, T. Solouki, Angew. Chem. Int. Ed. 52 (2013) 2426–2429.
[9] K. Ablajan, J. Mass Spectrom. 46 (2011) 77–84.
[10] J.L. Rummel, A.M. McKenna, A.G. Marshall, J.R. Eyler, D.H. Powell, Rapid Commun. Mass Spectrom. 24 (2010) 784–790.
[11] J. Laskin, J.H. Futrell, Mass Spectrom. Rev. 24 (2005) 135–167.
[12] E. Damoc, N. Youhnovski, D. Crettaz, J.D. Tissot, M. Przybylski, Proteomics 3 (2003) 1425–1433.
[13] T.B. Walk, A.W. Trautwein, H. Richter, G. Jung, Angew. Chem. Int. Ed. 38 (1999) 1763–1765.
[14] M. Wigger, J.R. Eyler, S.A. Benner, W. Li, A.G. Marshall, J. Am. Soc. Mass Spectrom. 13 (2002) 1162–1169.
[15] W. Wu, F. Song, C. Yan, Z. Liu, S. Liu, J. Pharmaceut. Biomed. 37 (2005) 437–446.
[16] J.L. Frahm, B.E. Howard, S. Heber, D.C. Muddiman, J. Mass Spectrom. 41 (2006) 281–288.
[17] M.M. Mapolelo, R.P. Rodgers, G.T. Blakney, A.T. Yen, S. Asomaning, A.G. Marshall, Int. J. Mass Spectrom. 300 (2011) 149–157.
[18] D.P. Kilgour, R. Wills, Y. Qi, P.B. O'Connor, Anal. Chem. 85 (2013) 3903–3911.
[19] E.N. Nikolaev, Y.I. Kostyukevich, G.N. Vladimirov, Mass Spectrom. Rev. (2014) 1–40.
[20] C.W. Landorf, M.M. Haley, Angew. Chem. Int. Ed. 45 (2006) 3914–3936.
[21] L.J. Wright, Dalton Trans. (2006) 1821–1827.
[22] J.R. Bleeke, Acc. Chem. Res. 40 (2007) 1035–1047.
[23] J. Chen, G. Jia, Coord. Chem. Rev. 257 (2013) 2491–2521.
[24] X.Y. Cao, Q. Zhao, Z. Lin, H. Xia, Acc. Chem. Res. 47 (2014) 341–354.
[25] E. Álvarez, M. Paneque, M.L. Poveda, N. Rendón, Angew. Chem. Int. Ed. 45 (2006) 474–477.
[26] M.A. Esteruelas, A.B. Masamunt, M. Oliván, E. Oñate, M. Valencia, J. Am. Chem. Soc. 130 (2008) 11612–11613.
[27] B. Liu, H. Xie, H. Wang, L. Wu, Q. Zhao, J. Chen, T.B. Wen, Z. Cao, H. Xia, Angew. Chem. Int. Ed. 48 (2009) 5461–5464.
[28] W.Y. Hung, B. Liu, W. Shou, T.B. Wen, C. Shi, H.H.Y. Sung, I.D. Williams, Z. Lin, G. Jia, J. Am. Chem. Soc. 133 (2011) 18350–18360.
[29] J. Chen, H.H.Y. Sung, I.D. Williams, Z. Lin, G. Jia, Angew. Chem. Int. Ed. 123 (2011) 10863–10866.
[30] C. Zhang, H. Zhang, A. Wei, X. He, H. Xia, Acta Chim. Sinica 71 (2013) 1373–1378.
[31] Á. Vivancos, M. Paneque, M.L. Poveda, E. Álvarez, Angew. Chem. Int. Ed. 52 (2013) 10068–10071.
[32] J. Chen, C. Zhang, T. Xie, T. Wen, H. Zhang, H. Xia, Organometallics 32 (2013) 3993–4001.
[33] C. Zhu, X.Y. Cao, H. Xia, Chin. J. Org. Chem. 33 (2013) 657–662.
[34] C. Zhu, M. Luo, Q. Zhu, J. Zhu, P.V.R. Schleyer, J.I. Wu, X. Lu, H. Xia, Nat. Commun. 5 (2014) 3265.
[35] C. Zhu, Q. Zhu, J. Fan, J. Zhu, X. He, X.Y. Cao, H. Xia, Angew. Chem. Int. Ed. 53 (2014) 3245.
[36] C. Zhu, S. Li, M. Luo, X. Zhou, Y. Niu, M. Lin, J. Zhu, Z. Cao, X. Lu, T. Wen, Z. Xie, P.V.R. Schleyer, H. Xia, Nat. Chem. 5 (2013) 698–703.
[37] B. Kanawati, K.P. Wanczek, Int. J. Mass Spectrom. 274 (2008) 30–47.
[38] J.F. de la Mora, G.J. Van Berkel, C.G. Enke, R.B. Cole, M. Martinez-Sanchez, J.B. Fenn, J. Mass Spectrom. 35 (2000) 939–952.