

# Modeling of the mass spectrum of dodecacarbonylo-triangulo-triosmium

Andrzej J. Gorączko

Received: 11 September 2010 / Accepted: 7 March 2011 / Published online: 27 April 2011  
© Springer-Verlag 2011

**Abstract** The present work attempts to predict the mass spectra of structures containing many clusters of doubly charged ions as well as singly charged ions. The method is applied to dodecacarbonylo-triangulo-triosmium,  $\text{Os}_3(\text{CO})_{12}$ , a particularly difficult example for modeling. The starting spectrum (25 points) can be reconstructed satisfactorily with 2% precision into a full form containing more than 400 peaks, which is consistent with the experimental form.

**Keywords** Mass spectrum modeling · Doubly charged ions · Computer assisted interpretation

## Introduction

Bradford and Nyholm obtained dodecacarbonylo-triangulo-triosmium,  $\text{Os}_3(\text{CO})_{12}$ , in good yields from the reaction of osmium tetroxide with carbon monoxide under high pressure [1, 2]. The chemical properties of  $\text{Os}_3(\text{CO})_{12}$  have been thoroughly examined [3, 4]. Direct reactions of ligands with the cluster often lead to complex product compositions because breaking the inert Os–CO bond requires high

temperatures, and at high temperatures the initially formed adducts react further successively.  $\text{Os}_3(\text{CO})_{12}$  is effectively converted to derivatives such as  $\text{Os}_3(\text{CO})_{11}(\text{MeCN})$  and  $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$  using  $\text{Me}_3\text{NO}$  as a decarbonylating agent [5]. The direct reaction of  $\text{Os}_3(\text{CO})_{12}$  with ethylene and pyridine results in the degradation of these organic ligands to give vinyl hydride  $\text{HOs}_3(\text{CO})_{10}(\eta^1, \eta^2\text{-C}_2\text{H}_3)$  and pyridyl-hydride  $\text{HOs}_3(\text{CO})_{10}(\text{NC}_5\text{H}_4)$ . These products illustrate the stability of the Os–H and Os–C bonds [6].

$\text{Os}_3(\text{CO})_{12}$  is a platform for examining the ways that hydrocarbons can interact with ensembles of metals. For example, in Fischer-Tropsch processing, it is understood that the poly-metallic catalysts used assist the hydrogenation of CO to give hydrocarbons [7]. Models for such intermediates are provided by the series  $\text{CH}_3(\text{H})\text{Os}_3(\text{CO})_{10}$ ,  $(\text{CH}_2)(\text{H})_2\text{Os}_3(\text{CO})_{10}$ , and  $(\text{CH})(\text{H})_3\text{Os}_3(\text{CO})_9$ . The molecule  $\text{CH}_3(\text{H})\text{-Os}_3(\text{CO})_{10}$  gave one of the first clear-cut examples of agostic bonding [8].

The present paper is an example of isotopomeric cluster modeling for the reconstruction of very complex mass spectra containing clusters related to singly charged ions and patterns corresponding to doubly charged ions.

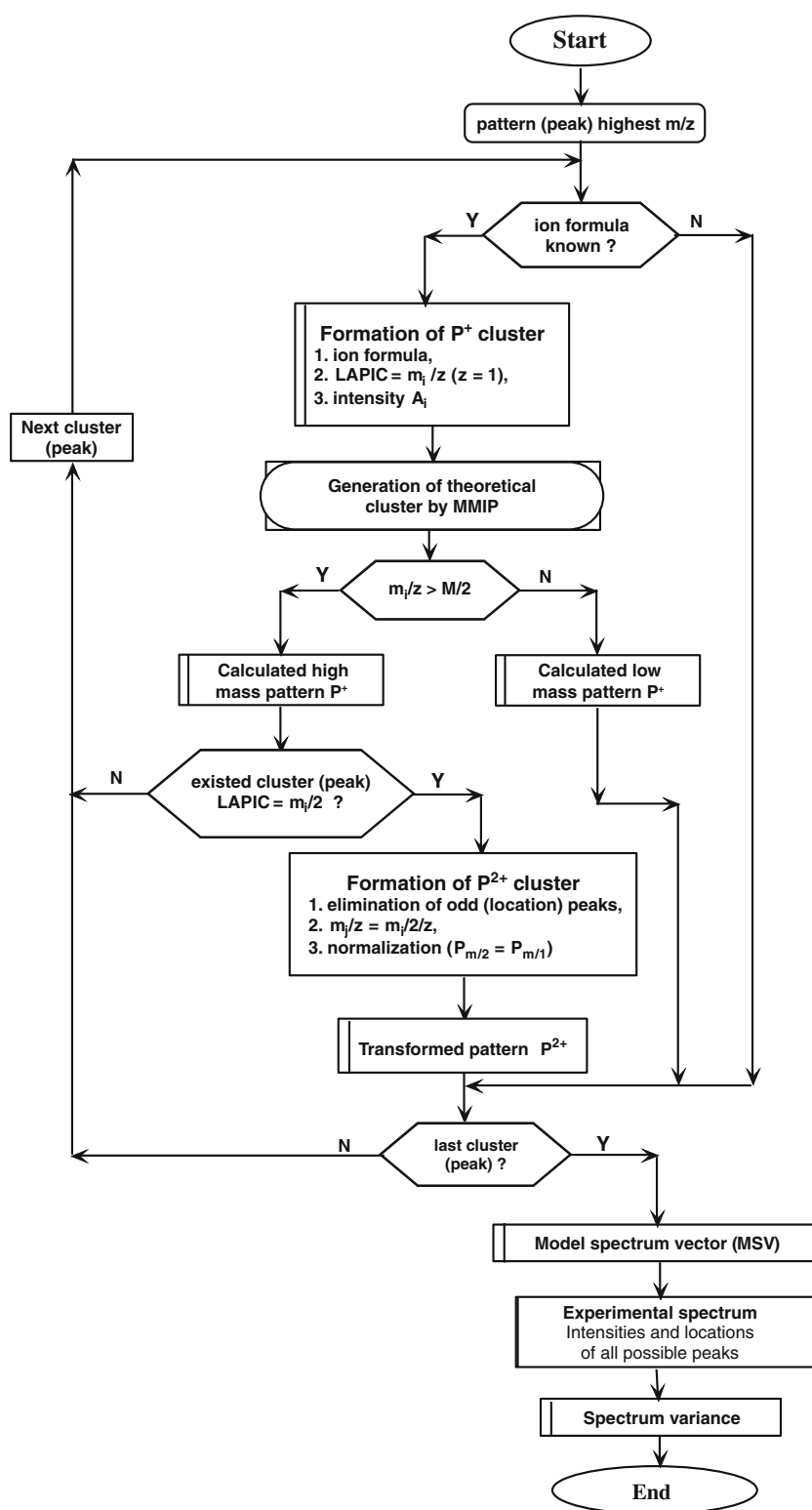
## Experimental

The mass spectrum of dodecacarbonylo-triangulo-triosmium  $\text{Os}_3(\text{CO})_{12}$  (Sigma-Aldrich #249742, 98%) was recorded by the Mass Spectrometry Laboratory, Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw. The EI mass spectra were recorded on an AMD-604, two-sector mass spectrometer (AMD Intecra, Harpstedt, Germany) of the B/E geometry with

A. J. Gorączko (✉)  
Department of Inorganic Chemistry,  
University of Technology and Life Science,  
Seminaryjna 3,  
85–326 Bydgoszcz, Poland  
e-mail: andygor@utp.edu.pl

A. J. Gorączko  
e-mail: uklejna@interia.pl

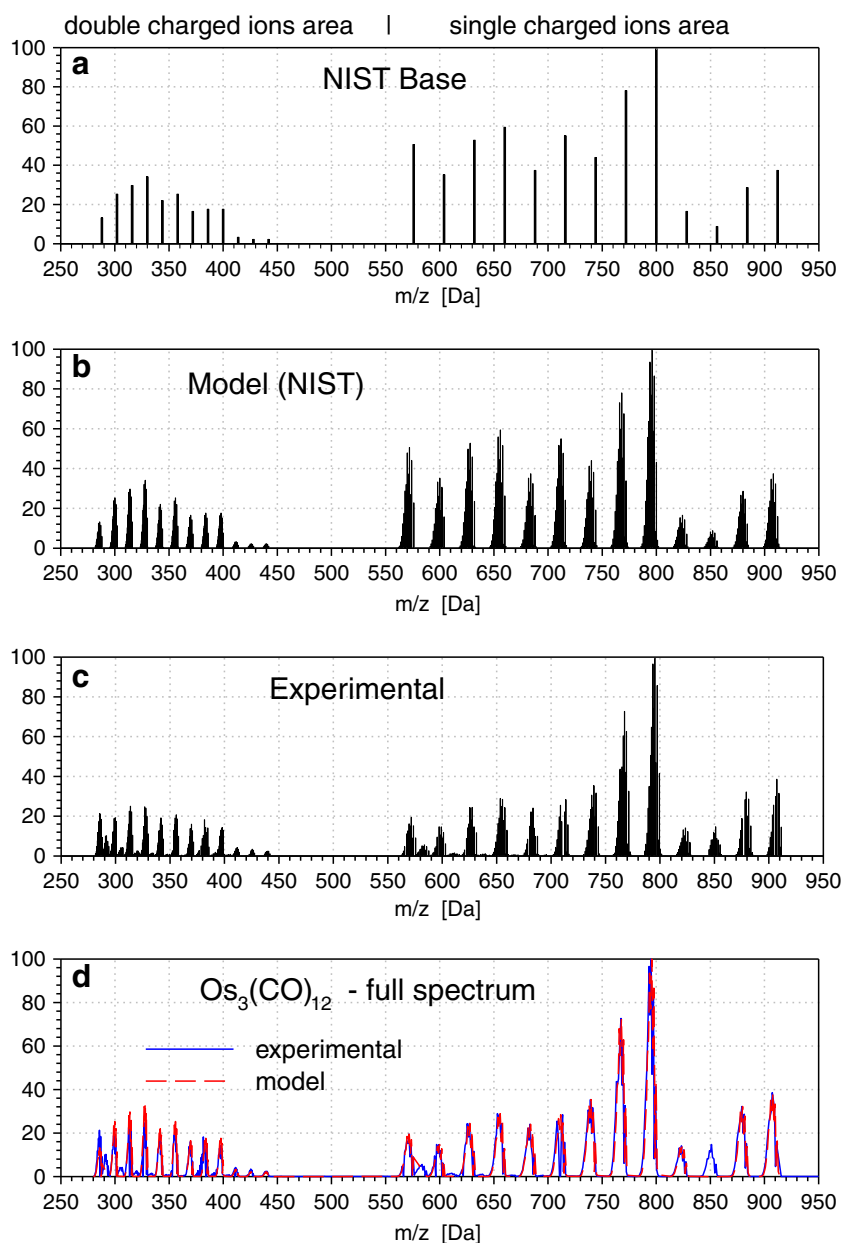
**Fig. 1** Modeling of mass spectra (MS) containing doubly charged ions



acceleration voltage of 8 kV, electron energy 70 eV and ion source temperature of 200°C. High-resolution data were obtained using a V/E high-resolution scan in relation

to perfluorokerosene, with an error lower than 10 ppm for all the ions discussed. The compounds were introduced by a direct insertion probe at temperatures of up to 300 °C.

**Fig. 2a–d** Mass spectra of dodecacarbonyltriangulo-triosmium,  $\text{Os}_3(\text{CO})_{12}$ . **a** Spectrum from MS-Database NIST-2000 [9]. **b** Spectrum model predicted from **a**. **c** Experimental spectrum. **d** Comparison of the experimental and model spectra



## Results

Mass spectrum of dodecacarbonylo-triangulo-triosmium,  $\text{Os}_3(\text{CO})_{12}$

The mass spectrum of  $\text{Os}_3(\text{CO})_{12}$  was investigated by Benzi et al. [9]. In the NIST-68 MS-Database it is presented in a previously simplified form [10, 11] containing 25 peaks only, as a composite of peaks of the highest intensity from each ionic cluster. The published spectrum [9, 11] can be applied to compound identification using the characteristic peaks; however, the isotopomeric analysis of this spectrum is impossible.

The presence of doubly charged ions usually goes unnoticed because their clusters are observed more rarely than those of singly charged ions [12]. The bands (clusters, patterns) connected with the doubly charged ions are located in the spectrum below  $M/2$ . In addition to overlapping with other bands, the narrow shapes of such patterns generate significant problems in their interpretation [13].

Doubly charged ions are observed in the mass spectra of  $\text{Os}_3(\text{CO})_{12}$ , and of their derivatives at different ionizing energy. The substitution of osmium atoms by ruthenium atoms [ $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{RuOs}_2(\text{CO})_{12}$  and  $\text{Ru}_2\text{Os}(\text{CO})_{12}$ ] decreased the energy of the ionizing electrons [9]. They follow

**Table 1** Adjustment of the model and experimental mass spectra of dodecacarbonyltriosmium, Os<sub>3</sub>(CO)<sub>12</sub>

P	P <sup>2+</sup> (low mass patterns)					P <sup>+</sup> (high mass clusters)				
	m/z [u]	I <sub>exp</sub> [%]	I <sub>model</sub> [%]	Points	Variance	m/z [u]	I <sub>exp</sub> [%]	Points	Variance	
Os <sub>3</sub>	285.7	21.24	19.45	15	1.03	571.5	19.45	14	0.77	
Os <sub>3</sub> (CO)	299.7	19.24	14.65	14	1.297	599.1	14.64	18	0.689	
Os <sub>3</sub> (CO) <sub>2</sub>	313.6	25.02	24.34	13	2.01	627.5	24.34	19	1.039	
Os <sub>3</sub> (CO) <sub>3</sub>	326.7	24.69	28.46	19	2.189	655.4	28.46	18	1.317	
Os <sub>3</sub> (CO) <sub>4</sub>	341.7	19.15	24.03	16	2.256	684.5	24.03	17	2.694	
Os <sub>3</sub> (CO) <sub>5</sub>	355.7	20.69	28.38	13	3.338	712.5	28.38	18	1.267	
Os <sub>3</sub> (CO) <sub>6</sub>	369.7	15.98	35.36	14	0.79	740.4	35.36	19	0.993	
Os <sub>3</sub> (CO) <sub>7</sub>	381.6	18.18	72.64	15	2.53	766.3	72.64	19	3.953	
Os <sub>3</sub> (CO) <sub>8</sub>	397.7	14.24	100	20	1.18	797.4	100	18	2.96	
Os <sub>3</sub> (CO) <sub>9</sub>	411.5	4.16	14.07	20	0.54	824.4	14.07	20	0.182	
Os <sub>3</sub> (CO) <sub>10</sub>	425.5	3.43	14.72	14	0.23	852.1	14.72	19	1.541	
Os <sub>3</sub> (CO) <sub>11</sub>	439.6	2.42	32.17	12	0.4	879.3	32.17	20	1.986	
Os <sub>3</sub> (CO) <sub>12</sub>						908.2	38.55	18	6.161	
all P <sup>2+</sup> clusters				185	1.472	all P <sup>+</sup> patterns		237	1.966	

a characteristic trend in which the highest charge is transported by fragments containing a number of carbonyl groups that increases with decreasing ionizing energy [14]. The mass spectrum of Fe<sub>3</sub>(CO)<sub>12</sub> contains very weak doubly charged species [8]. H<sub>2</sub>Os<sub>3</sub>(CO)<sub>12</sub> exhibits a behavior similar to that of Os<sub>3</sub>(CO)<sub>12</sub>, while Os<sub>3</sub>(CO)<sub>10</sub>Br<sub>2</sub> and Os<sub>3</sub>(CO)<sub>12</sub>Br<sub>2</sub> show that different structures do not appreciably affect the occurrence of doubly charged ions [15]. The marked increase in the stabilization of doubly charged species [9] observed in the mass spectra of Os<sub>3</sub>(CO)<sub>8</sub>[C<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub> shows the drastic influence of the organic ligands superimposed on that of the nature of metal atoms. In the mass spectrum of Os<sub>3</sub>(CO)<sub>8</sub>[C<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub> recorded at 70 eV, a rather strong peak of [M–8CO]<sup>3+</sup> was observed [16].

### Reconstruction of the mass spectrum

The complete mass spectrum of Os<sub>3</sub>(CO)<sub>12</sub> has not been published in the MS-Database [10] or in the literature [11]. It was constructed for compound identification rather than interpretation. The mass spectrum modeling is realized in three successive steps (Fig. 1):

1. The modeling of clusters related to singly charged ions is simple. Each isotopomeric pattern was predicted by Multiisotopomeric Modeling of Isotopic Patterns (MMIP) [17] on the basis of ion formula and abundances of natural isotopes [18]. After the calculations of the intensities of all the peaks of the cluster, the peaks were normalized to the intensity of the published signal representative of this cluster.

2. The prediction of patterns related to the doubly charged ions was more complex. At first the isotopomeric cluster of the singly charged ions (as described above) must be calculated. The peaks located at odd m/z values were removed. The remaining cluster was compressed by m/z = m/2z, and the intensities of the peaks contained in these patterns were then normalized using the peak from the published spectrum related to the band being calculated as the standard. The calculation method was presented at the recent conference “Modeling & Design of Molecular Materials” (MMDM '08, Wroclaw, Poland) [19, 20]
3. The construction of the final spectrum needs co-ligation of all fragments and addition of related clusters. At this stage, the previously described method [21] was applied.

The spectrum presented in Fig. 2a contains peaks of two groups:

1. 13 signals in the range above 550 Da relate to singly charged ions—the molecular M<sup>+</sup> and fragmental [M – n(CO)]<sup>+</sup> separated by 28 Da
2. 12 peaks located in the 280–460 Da area separated by 14 Da, possibly associated with doubly charged ions (excluding M<sup>2+</sup>).

The successive elimination of ligands is the dominating process in Os<sub>3</sub>(CO)<sub>12</sub> fragmentation, and thus the mass spectrum of dodecacarbonyltriosmium looks pure and simple. The simple structure of the compound provides

very good conditions for a precise determination of the mass spectrum.

The peak locations in the mass spectrum of dodecacarbonyltriangulo-triosmium indicate the presence of 13 clusters related to singly charged ions (molecular ion and 12 fragmentation ions) and 12 peaks corresponding to doubly charged ions (without  $M^{2+}$ ).

The final model is shown in Fig. 2b. The existence of the patterns connected with singly and doubly charged ions was revealed more effectively than in the simplified spectrum in Fig. 2a.

The calculations allow detection of a substantial error in peak location. In the database, the locations of peaks relevant to the doubly charged ions are shifted 2 Da down in comparison with the predicted locations, and the values remain the same for all +2 ions. In the areas of the singly charged ions, the differences are equal to 4 Da and are the same for all peaks. The incorrect values correspond to neither the average masses nor the nominal ones. Compensation by number of hydrogen atoms cannot be applied. This fact may be solely the result of errors in spectrometer calibration. The indicated discrepancies require measurement of the experimental spectrum of  $Os_3(CO)_{12}$  with careful calibration.

## Discussion

The experimental mass spectrum is presented in Fig. 2c. The spectra shown in Fig. 2b and c look similar; the similarity is also confirmed by Fig. 2d in which both spectra are compared. The calculation of variance by Biemann proposition [22] can be regarded as clear and objective;

in the range  $m/z > 500$  Da :

$$s_{singly}^2 = \frac{1}{v} \sum_{i=1}^v (P_{exp.i} - P_{calc.i})^2 \quad (1)$$

in the area  $m/z > 500$  Da:

$$s_{doubly}^2 = \frac{1}{w} \sum_{i=1}^w (P_{exp.i} - P_{transf.i})^2 \quad (2)$$

and finally the total variance of all spectra

$$s_{model}^2 = \frac{v \cdot s_{singly}^2 + w \cdot s_{doubly}^2}{v + w} \quad (3)$$

in which parameters  $v$  and  $w$  denote numbers of peaks occurring simultaneously in the model and in the experimental spectra  $P_{exp.i} \cdot P_{theo.i} > 0$  ( $P_{calc.i}, P_{transf.i} \rightarrow P_{theo.i}$ ). The variance should be established for singly ( $P_{calc.i}$ ) and doubly ( $P_{transf.i}$ ) charged ions separately because the prediction methods are different for the two ion types. Details of

the adjustment are shown in Table 1. Each pattern is represented by more than ten peaks and, therefore, it appears that the similarity is sufficient. Average variances,  $s^2=1.47$  for 185 peaks for the range of doubly charged ions, and  $s^2=1.97$  for 237 points in the singly charged ions area. These results should be treated as satisfactory in view of the difficulties of calibration of the spectrometer in the wide range 200–1,000 Da. The global adjustment looks very good:  $s^2=1.75$  for 422 peaks.

## Conclusions

The presented method of modeling the isotopomeric cluster enables reconstruction of the mass spectrum of  $Os_3(CO)_{12}$ , which was previously simplified by an unknown approach. The approach employed here appears to be an effective tool for complex-spectrum-containing clusters of both singly- and doubly-charged ions. In conclusion, it is evident that the model presented generates a reconstituted spectrum in perfect agreement with the experimental picture.

## References

- Bradford CW, Nyholm RS, (1967), An improved method for the preparation of  $Os_3(CO)_{12}$ , and some derivatives. Chem Commun (London) 1967:384–385
- Johnson BFG, Lewis J, Kilty PA (1968) Chemistry of polynuclear compounds XIII The preparation and some reactions of dodecacarbonyltriostmium. J Chem Soc A 1968:2859–2864
- Corey ER, Dahl LF (1962) The molecular and crystal structure of  $Os_3(CO)_{12}$ . Inorg Chem 1:521–526
- Pauling L (1976) Metal-metal bond lengths in complexes of transition metals (valence bonds/resonating bonds/metal carbonyls/spd hybrid orbitals). Proc Natl Acad Sci USA 73:4290–4293
- Keister JB, Shapley JR (1982) Solution structures and dynamics of complexes of  $H_2Os_3(CO)_{10}$  with Lewis bases. Inorg Chem 21:3304–3310
- Calvert RB, Shapley JR (1978) Decacarbonyl-(methyl) hydrotriosmium: NMR evidence for a carbon hydrogen-osmium interaction. J Am Chem Soc 100:7726–7727
- Steinmetz GR, Morrison ED, Geoffrey GL (1984) Trinuclear osmium clusters as models for intermediates in carbon monoxide reduction chemistry. 1 stepwise reduction of CO to a P-CH ligand on an  $Os_3$  cluster face. J Am Chem Soc 106:2559–2564
- Wheeler RA, Hoffmann R (1986) A new magic cluster electron count and metal-metal multiple bonding. J Am Chem Soc 108:6605–6610
- Benzi PP, Michelin-Lauserot L, Operti GA, Vaglio M, Valle P, Volpe (1988) Multiply charged ions in the mass spectra of trinuclear carbonyl metal compounds and their derivatives. Inorg Chim Acta 145:99–103
- $C_{12}O_{12}Os_3$  – NIST-2000 # 18778 CAS, #15696409, Johnson BFG, Department of Chemistry, University of Manchester, UK, (AEI/GEC MS-9)
- Lewis J, Manning AR, Miller JR, Wilson JM (1966)  $Os_3(CO)_{12}$  Chemistry of polynuclear compounds Part VII. The mass spectra of some polynuclear metal carbonyl complexes. J Chem Soc A 1966:1663–1670

12. Smith RM, Busch KL (1999) Understanding mass spectra—a basic approach. Wiley, New York, pp 46–48
13. Gorączko AJ (2007) Isotope patterns. In: Gross ML, Caprioli RM (eds) Encyclopedia of mass spectrometry, vol 6. Elsevier, Amsterdam, pp 62–76
14. Johnson BF, Lewis J, Williams IG, Wilson JM (1967) Mass spectra of inorganic molecules, Part II. Some polynuclear transition-metal carbonyl. *J Chem Soc A* 1967:341–344
15. Vaglio GA (1979) Negative ion mass spectra of  $\text{Os}_3(\text{CO})_{12}\text{X}_2$  and  $\text{Os}_3(\text{CO})_{10}\text{X}_2$  complexes ( $\text{X}=\text{Br I}$ ). *J Organomet Chem* 169:83–85
16. Gambino O, Vaglio GA, Ferrari RP, Cetini G (1971) Acetylenic derivatives of metal carbonyls XII. Diphenylacetylenic derivatives of dodecacarbonyltriosmium. *J Organomet Chem* 30:381–390
17. Goraczko AJ, Szymura JA (2001) Multiisotopic modelling of mass spectra: a procedure for verification of the fragmentation hypothesis for the organometallic and coordination compounds. *Comput Chem* 25:559–568
18. Isotopic Abundances of the Elements, Washington University, St Louis, <http://presolar.wustl.edu/ref/IsotopeAbundanceTable.pdf>
19. Goraczko AJ (2008) Prediction of double-charge ion pattern of high- and low-resolution isotopomeric forms. In: Proceedings of International Conference on Modeling & Design of Molecular Materials—MMDM 2008. 23–28 June 2008, Piechowice, Poland
20. Goraczko AJ (2009) Prediction of the doubly charged ion pattern by modeling of the high- and low-resolution mass spectra of isotopomeric forms. *J Mol Model* 15:759–764
21. Gorączko AJ, Szymura JA (2001) Multiisotopic modeling of mass spectra: a procedure for verification of the fragmentation hypothesis for the organometallic and coordination compounds. *Comput Chem* 25:559–568
22. Biller JE, Biemann K (1974) Reconstructed mass spectra. A novel approach for the utilization of gas chromatograph—mass spectrometer data. *Anal Lett* 7:515–528