

Note

ToF-SIMS analysis of surface-anchored organometallic clusters

Chunxiang Li ^a, Mei Ying Doreen Lai ^b, Weng Kee Leong ^{a,*}

^a Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260, Singapore

^b Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, Singapore

Received 5 April 2005; received in revised form 5 May 2005; accepted 9 May 2005

Available online 16 June 2005

Abstract

ToF-SIMS analysis of the organometallic cluster $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-SCH}_2\text{CH}_2\text{SH})$ chemically attached onto a silver or gold surface, and of the cluster fragment $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-OSi}\equiv)$ on a silica surface, allows for identification of the surface organometallic species, and also gives information on its reactivity.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Organometallic; Clusters; ToF-SIMS; Surface

The interaction of organometallic clusters and surfaces encompasses interests in the employment of organometallic clusters as precursors for the deposition of molecular clusters [1] and size-controlled metallic particles [2], as well as in surface-mediated syntheses of organometallic clusters [3,4]. The chief difficulty in examining such surface-deposited species is the availability of suitable characterisation methods. Methods available for the characterization of surface-anchored organometallic clusters include solid-state IR spectroscopy, surface-enhanced Raman spectroscopy (SERS), X-ray photoelectron spectroscopy (XPS), EXAFS, and various microscopy techniques such as AFM, SEM, TEM and STM. Among these, XPS is useful in identifying the elements present; EXAFS may afford some idea of the geometry of the surface-anchored species but it is notoriously difficult to interpret; the microscopy techniques have limited use as far as characterization of molecular species is concerned since information obtainable about the ligands is limited. The latter information can in principle be obtainable from infrared spectroscopy. However, acquisition of IR data on metallic sur-

faces is not easy, even with SERS. Insofar as clusters are concerned, there is also uncertainty about the nuclearity of the clusters, and if the surface species does not have molecular analogues, the IR data may be impossible to interpret.

We have recently wanted to anchor organometallic clusters onto various surfaces and sought a mass spectrometry technique that would afford us information about the size and composition of the surface-deposited species. One of the useful mass spectrometric methods for the characterisation of surfaces is Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), which has been applied to metals and inorganic compounds [5], ultrathin films [6], self-assembled monolayers [7], and even biomaterial surfaces [8]. We would like to report here that ToF-SIMS appears to be a very powerful method that can yield useful information on the surface-anchored organometallic species.

The cluster $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-SCH}_2\text{CH}_2\text{SH})$ [9], was anchored onto both silver and gold surfaces [10]. The ToF-SIMS spectra of these surfaces show very clearly the molecular fragment $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-S})$ [11], together with the expected fragments due to sequential loss of CO (Fig. 1). That the most obvious highest m/z fragment corresponds to $[\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu\text{-S})]^+$,

* Corresponding author. Tel.: +65 68745131; fax: +65 67791691.

E-mail address: chmlwk@nus.edu.sg (W.K. Leong).

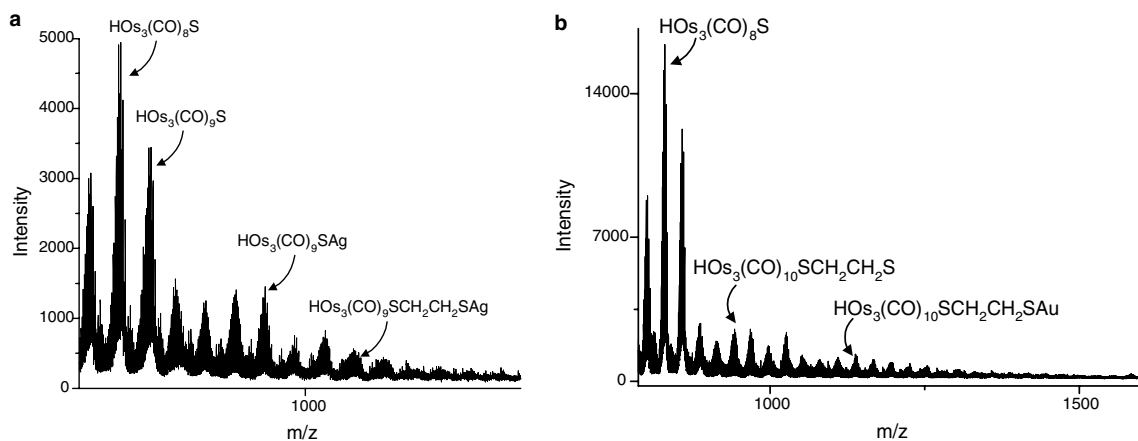


Fig. 1. ToF-SIMS (positive ion mode) spectra of $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-SCH}_2\text{CH}_2\text{SH})$ anchored onto: (a) silver foil and (b) gold foil.

together with presence of fragments such as $[\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu\text{-S})\text{Ag}]^+$, is consistent with observations that the C–S bond in such cluster species can be fairly easily cleaved [12].

Higher molecular weight fragments attributable to $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-SCH}_2\text{CH}_2\text{S})]^+$ and even $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-SCH}_2\text{CH}_2\text{SM})]^+$ (where M = Ag or Au) may be discerned although the intensities are rather low; the spectra were similar whether acquired in the positive or negative modes. A consequence of the high energy of the sputtering beam is the observation of fragments with even higher m/z , attributable to fragments from ions containing more than one surface metal atom, i.e., $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-SCH}_2\text{CH}_2\text{SM}_n)]^+$ ($n > 1$).

The ToF-SIMS of $\text{Os}_3(\text{CO})_{12}$ coated onto a gold surface, i.e., without washing of the surface, shows the molecular mass fragment and its attendant fragmentation pattern. This result is similar to an earlier report on the cluster $[\text{Ru}_5\text{C}(\text{CO})_{14}\text{Pt}(\text{C}_8\text{H}_{12})]$ [13]. On the other hand, silver and gold foils treated with $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$, using an identical procedure to that used for our $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-SCH}_2\text{CH}_2\text{SH})$ sample above, did not show any detectable signals attributable to the parent clusters or their fragments. This served to verify that the signals we have obtained above were not due to physisorbed species which may not have been adequately removed during sample preparation.

It would be particularly useful if the technique can be applied to organometallic species supported on silica as this is a very common support employed in catalysis and surface-mediated syntheses. We have thus carried out a ToF-SIMS analysis of the surface-anchored cluster species $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-OSi}\equiv)$ (where $\text{Si}\equiv$ represents the silica surface), which we prepared by soaking a glass plate in a solution of $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-OH})$ [14]. This surface-anchored species has been extensively characterized [4]. Despite the expectedly low concentration of this

species, the cluster fragment $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}]^+$ (cluster of peaks around m/z 851) can still be discerned (Fig. 2) [15]. A molecular fragment corresponding to $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-O})]^+$ is not observed although the fragment $[\text{Os}_3(\mu\text{-H})(\text{CO})_8(\mu\text{-O})]^+$ corresponding to subsequent loss of two CO ligands from it is discernible (cluster of peaks at about m/z 813). This would suggest that the cleavage of the Os–O bond is more facile than that of the O–Si bond, which is consistent with the suggested mechanism for the formation of $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-OH})$ from the reaction of $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-OSi}\equiv)$ with water [4].

ToF-SIMS is thus not only a very useful method for the analysis of surface-anchored organometallic species, but is also able to provide some information on the likely chemistry of this species. We believe that the utility of ToF-SIMS for the characterization of surface-anchored species is vast and not confined to organometallic cluster species only, and we are currently exploring the scope of this application.

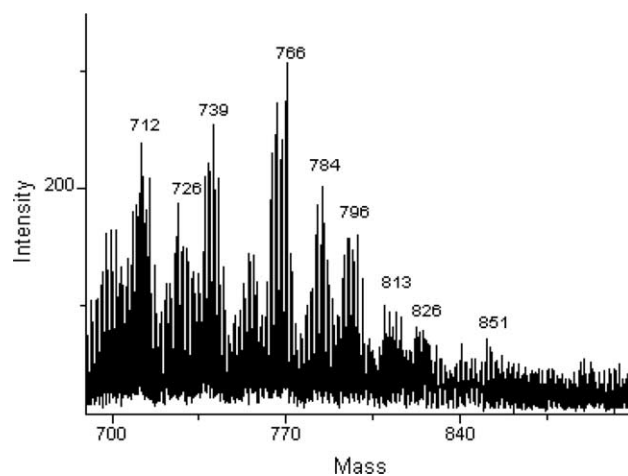


Fig. 2. ToF-SIMS (positive ion mode) spectrum of $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-OSi}\equiv)$.

Acknowledgement

This work was supported by an A*STAR grant (Research Grant No. 022 109 0061) and one of us (C.L.) thanks the University for a Research Scholarship.

References

- [1] For examples, see: (a) M. Abe, T. Michi, A. Sato, T. Kondo, W. Zhou, S. Ye, K.Y. Uosaki, Y. Sasaki, *Angew. Chem. Int. Ed.* 42 (2003) 2912; (b) A. Morneau, A. Manivannan, C.R. Cabrera, *Langmuir* 10 (1994) 3940; (c) D. Li, L.W. Moore, B.L. Swanson, *Langmuir* 10 (1994) 1177; (d) S.E. Deutsch, J.R. Chang, B.C. Gates, *Langmuir* 9 (1993) 1284; (e) S. Yamamoto, R.M. Lewis, Y. Nabata, H. Hotta, H. Kuroda, *Inorg. Chem.* 29 (1990) 4342; (f) S. Yamamoto, R.M. Lewis, H. Hotta, H. Kuroda, *Vacuum* 41 (1990) 65; (g) J.J. Venter, M.A. Jeremy, *J. Mol. Catal.* 56 (1989) 117; (h) C. Dossi, A. Fusi, E. Grilli, R. Psaro, R. Ugo, R. Zaroni, *Catal. Today* 2 (1988) 585; (i) B.M. Choudary, K.R. Kumar, *Appl. Catal.* 35 (1987) 177; (j) S.C. Brown, J. Evans, *J. Chem. Soc., Chem. Commun.* (1978) 1063.
- [2] For examples, see: (a) R. Ugo, C. Dossi, R. Psaro *J. Mol. Catal. A* 107 (1996) 13; (b) Y. Chi, H.-L. Yu, W.-L. Ching, C.-S. Liu, Y.-L. Chen, T.-Y. Chou, S.-M. Peng, G.-H. Lee, *J. Mat. Chem.* 12 (2002) 1363.
- [3] (a) E. Cariati, C. Dragonetti, D. Roberto, R. Ugo, E. Lucenti, *Inorg. Chim. Acta* 349 (2003) 189; (b) R. Giordano, P. Serp, P. Kalck, Y. Kihn, J. Schreiber, C. Marhic, J.-L. Christiane, *Eur. J. Inorg. Chem.* (2003) 610; (c) E. Lucenti, D. Roberto, C. Roveda, R. Ugo, E. Cariati, *J. Cluster Sci.* 12 (2001) 113; (d) E. Cariati, D. Roberto, R. Ugo, *J. Cluster Sci.* 9 (1998) 329; (e) E. Cariati, P. Recanati, D. Roberto, R. Ugo, *Organometallics* 17 (1998) 1266; (f) D. Roberto, E. Cariati, E. Lucenti, M. Respini, R. Ugo, *Organometallics* 16 (1997) 4531; (g) D. Roberto, E. Cariati, R. Ugo, R. Psaro, *Inorg. Chem.* 35 (1996) 2311; (h) D. Roberto, E. Cariati, R. Psaro, R. Ugo, *Organometallics* 13 (1994) 734; (i) S. Kawi, Z. Xu, B.C. Gates, *Inorg. Chem.* 33 (1994) 503; (j) D. Roberto, R. Psaro, R. Ugo, *Organometallics* 12 (1993) 2292; (k) H.H. Lamb, B.C. Gates, *J. Phys. Chem.* 96 (1992) 1099; (l) J. Puga, R. Patrini, K.M. Sanchez, B.C. Gates, *Inorg. Chem.* 30 (1991) 2479; (m) H.H. Lamb, A.S. Fung, P.A. Tooley, J. Puga, T.R. Krause, M.J. Kelley, B.C. Gates, *J. Am. Chem. Soc.* 111 (1989) 8367; (n) A.S. Fung, P.A. Tooley, M.J. Kelley, B.C. Gates, *J. Chem. Soc., Chem. Commun.* (1988) 371.
- [4] (a) C. Dragonetti, E. Lucenti, D. Roberto, *Inorg. Synth.* 34 (2004) 215; (b) D. Roberto, E. Lucenti, C. Roveda, R. Ugo, *Organometallics* 16 (1997) 5974; (c) E. Cariati, D. Roberto, R. Ugo, *Gazz. Chim. Ital.* 126 (1996) 339; (d) C. Dossi, A. Fusi, M. Pizzotti, R. Psaro, *Organometallics* 9 (1990) 1994; (e) C. Dossi, R. Psaro, R. Zaroni, F.S. Stone, *Spectrochim. Acta A* 43A (1987) 1507–1510; (f) B. Besson, B. Moraweck, A.K. Smith, J.M. Basset, R. Psaro, A. Fusi, R. Ugo, *J. Chem. Soc., Chem. Commun.* (1980) 569; (g) A.K. Smith, B. Besson, J.M. Basset, R. Psaro, A. Fusi, R. Ugo, *J. Organomet. Chem.* 192 (1980) C31.
- [5] Z. Li, K. Hirokawa, *Anal. Sci.* 19 (2003) 1231.
- [6] Z. Li, R.D. Rickman, S.V. Verkhoturov, E.A. Schweikert, *Appl. Surf. Sci.* 231 (2004) 328.
- [7] A. Hooper, G.L. Fisher, K. Konstadinidis, D. Jung, H. Nguyen, R. Opila, R.W. Collins, N. Winograd, D.L. Allara, *J. Am. Chem. Soc.* 121 (1999) 8052.
- [8] A.M. Belu, D.J. Graham, D.G. Castner, *Biomaterials* 24 (2003) 3635.
- [9] K.M. Hanif, S.E. Kabir, M.A. Mottalib, M.B. Hursthouse, K.M.A. Malik, E. Rosenberg, *Polyhedron* 19 (2000) 1073.
- [10] A glass slide coated with a thin film of gold was soaked in a dichloromethane solution (5 ml) of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-SCH}_2\text{-CH}_2\text{SH})$ (3 mg) for 2 d, washed with dichloromethane, and then dried in vacuo for 8 h.
- [11] The ToF-SIMS spectra were recorded on an ION-TOF SIMS 4 instrument, using bunched $^{69}\text{Ga}^+$ ion pulses with impact energy of 25 keV.
- [12] (a) R.D. Adams, J.E. Babin, *New J. Chem.* 12 (1988) 641; (b) J. Evans, B.P. Gracey, *J. Chem. Res., Synopses* (1986) 42; (c) R.D. Adams, I.T. Horvath, P. Mathur, B.E. Segmueller, *Organometallics* 2 (1983) 996.
- [13] A. Delcorte, S. Hermans, M. Devillers, N. Lourette, F. Aubriet, J.-F. Muller, P. Bertrand, *Appl. Surf. Sci.* 231–232 (2004) 131.
- [14] The glass slide was soaked in a dichloromethane solution of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})$ at ambient temperature for 1 d, washed several times with dichloromethane, and then air-dried.
- [15] Similar results were obtained with a glass slide refluxed in an octane solution of $\text{Os}_3(\text{CO})_{12}$.