

UV laser desorption/ionisation mass spectrometry of the triruthenium clusters $\text{Ru}_3(\text{CO})_{12-n}(\text{PPh}_3)_n$ ($n = 1, 2$ and 3)

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Abstract

The negative ion ultraviolet laser desorption mass spectra of $\text{Ru}_3(\text{CO})_{12}$ and its triphenylphosphine derivatives $\text{Ru}_3(\text{CO})_{12-n}(\text{PPh}_3)_n$ ($n = 1-3$) have been recorded using laser desorption/ionisation time-of-flight mass spectrometry (LDI-TOF-MS). The spectra contain peaks in the parent region together with peaks at higher masses due to extensive gas phase reactions. Substitution of one to three carbonyls by the bulky triphenylphosphine ligand has a number of interesting effects on the spectra, most notably, increasing the degree of coordinative unsaturation of the gas phase clusters in the molecular ion region and increasing the intensity of the subsequent high mass reaction products. © 1999 Elsevier Science S.A. All rights reserved.

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The characterisation of transition metal carbonyl clusters relies heavily on single crystal X-ray diffraction [1]. The emphasis on X-ray diffraction has introduced a bias into the field in that it is often only clusters that provide single crystals that are satisfactorily characterised. In an effort to address this imbalance, a range of mass spectrometric techniques has been applied to the study of clusters with varying degrees of success, including plasma desorption [2,3], fast atom bombardment [4], electrospray ionisation [5] and laser desorption/ionisation mass spectrometry [6], and this area has been recently reviewed [7]. Laser desorption/ionisation of neutral metal carbonyl clusters initiates gas phase reactions that result in extensive aggregation of the precursor clusters to form much larger clusters, complicating the assignment of the parent molecule [8]. Often the peaks in the parent ion region are of lower intensity than those of the cluster aggregate peaks and in some cases they are not even observed. The gas phase chemistry induced by the laser desorption/ionisation process is interesting in its own right and is not yet fully understood, although the trinuclear clusters $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}$ and Os) have been studied in some detail [9]. Aggregation of

carbonyl clusters in the gas phase has also been observed in electron impact ionisation FTICR mass spectrometry [10,11]. Similar extended clustering has also been seen in plasma desorption spectra [2,3].

This paper explores the effect that replacing one, two and three of the carbonyl ligands in $\text{Ru}_3(\text{CO})_{12}$ for the bulky triphenylphosphine ligand has on their spectra, thereby providing further insight into the gas phase chemistry that takes place in the laser desorption/ionisation process. Experiments were performed using a Kratos Kompact MALDI-4 time-of-flight mass spectrometer¹.

The negative ion LDI-TOF mass spectra of $\text{Ru}_3(\text{CO})_{12}$ (**1**) and $\text{Ru}_3(\text{CO})_{12-n}(\text{PPh}_3)_n$ ($n = 1$ (**2**), 2 (**3**) and 3 (**4**)) are shown in Fig. 1 (a)–(d). Peak centroids are listed in Table 1 together with the corresponding assignments. The spectrum of **1** has been reported previously and was described at length

¹ The compounds $\text{Ru}_3(\text{CO})_{12}$ (**1**) [12] and $\text{Ru}_3(\text{CO})_{12-n}(\text{PPh}_3)_n$ ($n = 1$ (**2**), 2 (**3**) and 3 (**4**)) [13] were prepared according to the literature methods. Samples were dissolved in dichloromethane and deposited directly onto the sample slide. The sample was allowed to evaporate and several layers were applied leaving a thin layer. The sample was analysed using a Kratos Kompact MALDI-4 mass spectrometer. Laser intensities were held constant at a mid-range value for all four samples investigated. The instrument was operated in linear mode. The data from 50 successive shots were averaged to improve the signal-to-noise ratio.

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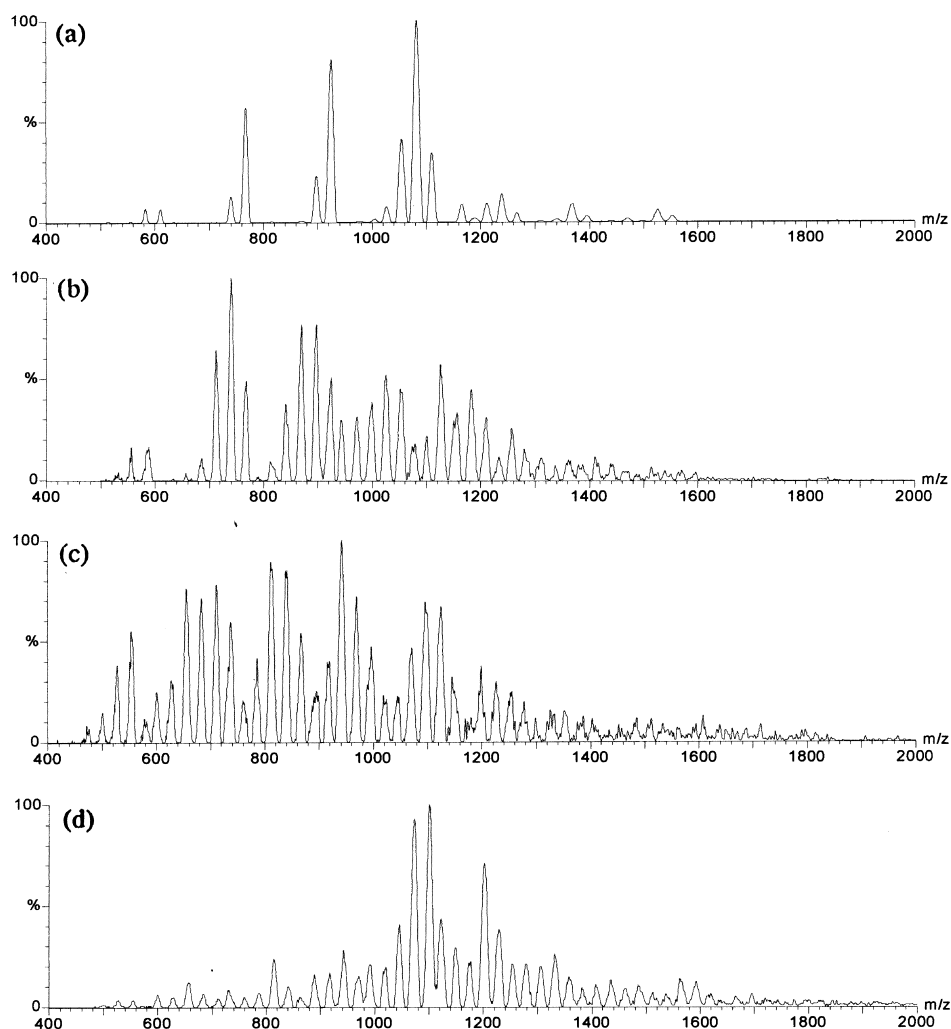


Fig. 1. The negative ion spectra of (a) $\text{Ru}_3(\text{CO})_{12}$ (**1**), (b) $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_3)$ (**2**), (c) $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$ (**3**) and (d) $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ (**4**).

[9]. Some general features have emerged from a comparison of the spectrum of **1** with the spectra of compounds **2–4**.

1. The PPh_3 ligands are not coordinated to any of the clusters in the spectra; only homoleptic ruthenium carbonyl clusters are observed. As such, the highest intensity peak for each cluster in the parent ion region depends upon the number of PPh_3 ligands present in the precursor cluster.
2. In addition to all the PPh_3 ligands being stripped from the cluster, one or more CO ligands are always lost for the clusters in the molecular ion region.
3. As the number of phosphine ligands in the parent cluster increases the extent of fragmentation, gas phase aggregation products also increase. As expected, there is an overall increase in nuclearity of the cluster species produced.

The triphenylphosphine ligand is a considerably more bulky and a less effectively coordinating ligand than CO. As such, it is not surprising that it dissociates before CO upon laser ablation. What is surprising is that electron capture in **2–4** also requires loss of CO. It has previously been pointed out that electron attachment in $\text{Ru}_3(\text{CO})_{12}$ (**1**) must be accompanied by loss of one CO ligand and therefore the

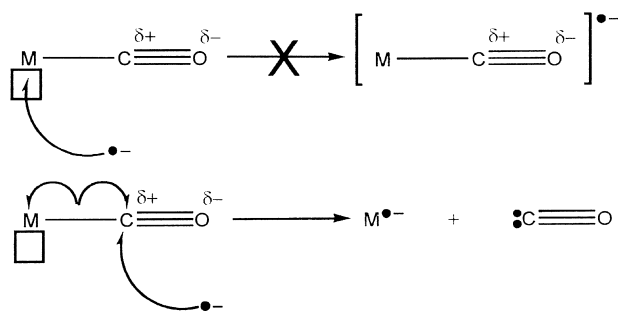
highest mass observed in the parent region is for $[\text{Ru}_3(\text{CO})_{11}]^-$ [9]. In other words, the electronically saturated cluster $\text{Ru}_3(\text{CO})_{12}$ cannot accept an electron without losing a CO ligand. From this observation it would follow that in compounds **2–4**, where the triphenylphosphine ligands are more labile, electron attachment could take place without CO loss being required, i.e. the highest mass peak in the parent region for $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_3)$ should be $[\text{Ru}_3(\text{CO})_{11}]^-$ as the single electron should be able to be accommodated by the unsaturated cluster. However, $[\text{Ru}_3(\text{CO})_{10}]^-$ is the highest mass peak in the parent region, which suggests that electron attachment may involve initial nucleophilic attack at a carbonyl ligand (see Scheme 1).

The most notable difference between the spectra that are shown in Fig. 1 is that considerably more fragmentation and gas phase reaction products are observed for the triphenylphosphine derivatised clusters **2–4** than for **1**. This enhanced reactivity is expected, as the initial loss of a larger number of ligands, viz. the triphenylphosphines and one carbonyl, means that the clusters are considerably more electronically unsaturated and subsequently less stable. These highly reactive species are more likely to aggregate to form larger clus-

Table 1
Peak maxima for principal envelopes in the negative ion UV laser desorption/ionisation mass spectra of compounds 1–4

| Peak centroids | Formula of ions | Relative intensity (%) | | | | Calculated weight |
|----------------|--|------------------------|--------------|--------------|--------------|-------------------|
| | | 1 | 2 | 3 | 4 | |
| 472 | [Ru ₃ (CO) ₆] ⁻ | – | – | 7 | – | 472.7 |
| 500 | [Ru ₃ (CO) ₇] ⁻ | – | – | 13 | – | 500.7 |
| 528 | [Ru ₃ (CO) ₈] ⁻ | – | 4 | 38 | 4 | 528.7 |
| 556 | [Ru ₃ (CO) ₉] ⁻ | – | 16 | 55 | 4 | 556.7 |
| 585 | [Ru ₃ (CO) ₁₀] ⁻ | 6 | 17 | – | – | 584.7 |
| 611 | [Ru ₃ (CO) ₁₁] ⁻ | 7 | – | – | – | 612.7 |
| 574 | [Ru ₄ (CO) ₆] ⁻ | – | – | 12 | – | 573.6 |
| 602 | [Ru ₄ (CO) ₇] ⁻ | – | – | 25 | 7 | 601.6 |
| 630 | [Ru ₄ (CO) ₈] ⁻ | – | – | 31 | 5 | 629.6 |
| 658 | [Ru ₄ (CO) ₉] ⁻ | – | 4 | 75 | 13 | 657.6 |
| 686 | [Ru ₄ (CO) ₁₀] ⁻ | – | 11 | 72 | 6 | 685.7 |
| 712 | [Ru ₄ (CO) ₁₁] ⁻ | – | 64 | 77 | 4 | 713.6 |
| 739 | [Ru ₄ (CO) ₁₂] ⁻ | 12 | 100 | 58 | – | 741.6 |
| 767 | [Ru ₄ (CO) ₁₃] ⁻ | 57 | 58 | – | – | 769.6 |
| 729 | [Ru ₅ (CO) ₈] ⁻ | – | – | – | 10 | 729.4 |
| 756 | [Ru ₅ (CO) ₉] ⁻ | – | – | 23 | 4 | 757.4 |
| 784 | [Ru ₅ (CO) ₁₀] ⁻ | – | 3 | 42 | 7 | 785.4 |
| 812 | [Ru ₅ (CO) ₁₁] ⁻ | – | 9 | 88 | 24 | 813.4 |
| 840 | [Ru ₅ (CO) ₁₂] ⁻ | – | 37 | 84 | 10 | 841.4 |
| 868 | [Ru ₅ (CO) ₁₃] ⁻ | 2 | 76 | 54 | – | 869.4 |
| 899 | [Ru ₅ (CO) ₁₄] ⁻ | 24 | 76 | – | – | 897.5 |
| 927 | [Ru ₅ (CO) ₁₅] ⁻ | 82 | 51 | – | – | 925.5 |
| 862 | [Ru ₆ (CO) ₉] ⁻ | – | – | – | 5 | 859.4 |
| 889 | [Ru ₆ (CO) ₁₀] ⁻ | – | – | – | 16 | 887.4 |
| 913 | [Ru ₆ (CO) ₁₁] ⁻ | – | – | 40 | 16 | 915.4 |
| 941 | [Ru ₆ (CO) ₁₂] ⁻ | – | 30 | 100 | 27 | 943.4 |
| 969 | [Ru ₆ (CO) ₁₃] ⁻ | – | 32 | 72 | 15 | 971.4 |
| 997 | [Ru ₆ (CO) ₁₄] ⁻ | 2 | 38 | 46 | – | 999.4 |
| 1025 | [Ru ₆ (CO) ₁₅] ⁻ | 4 | 52 | 24 | – | 1027.4 |
| 1053 | [Ru ₆ (CO) ₁₆] ⁻ | 42 | 55 | – | – | 1055.4 |
| 1081 | [Ru ₆ (CO) ₁₇] ⁻ | 100 | 17 | – | – | 1083.4 |
| 1109 | [Ru ₆ (CO) ₁₈] ⁻ | 35 | – | – | – | 1111.3 |
| 991 | [Ru ₇ (CO) ₁₂] ⁻ | – | – | – | 22 | 988.3 |
| 1016 | [Ru ₇ (CO) ₁₁] ⁻ | – | – | – | 20 | 1016.3 |
| 1045 | [Ru ₇ (CO) ₁₂] ⁻ | – | – | 23 | 40 | 1044.3 |
| 1073 | [Ru ₇ (CO) ₁₃] ⁻ | – | – | 55 | 92 | 1072.3 |
| 1100 | [Ru ₇ (CO) ₁₄] ⁻ | – | 22 | 68 | 100 | 1100.3 |
| 1127 | [Ru ₇ (CO) ₁₅] ⁻ | – | 56 | 66 | 44 | 1128.2 |
| 1154 | [Ru ₇ (CO) ₁₆] ⁻ | 9 | 33 | 32 | 29 | 1156.2 |
| 1182 | [Ru ₇ (CO) ₁₇] ⁻ | 4 | 45 | 12 | 23 | 1184.2 |
| 1213 | [Ru ₇ (CO) ₁₈] ⁻ | 10 | 31 | – | – | 1212.2 |
| 1239 | [Ru ₇ (CO) ₁₉] ⁻ | 15 | – | – | – | 1240.2 |
| 1266 | [Ru ₇ (CO) ₂₀] ⁻ | 5 | – | – | – | 1268.2 |
| 1198 | [Ru ₈ (CO) ₁₄] ⁻ | – | – | 36 | 71 | 1201.1 |
| 1231 | [Ru ₈ (CO) ₁₅] ⁻ | – | 12 | 28 | 38 | 1229.1 |
| 1259 | [Ru ₈ (CO) ₁₆] ⁻ | – | 25 | 25 | 22 | 1257.1 |
| 1287 | [Ru ₈ (CO) ₁₇] ⁻ | – | 14 | 20 | ^a | 1285.1 |
| 1316 | [Ru ₈ (CO) ₁₈] ⁻ | 1 | 11 | ^a | – | 1313.1 |
| 1344 | [Ru ₈ (CO) ₁₉] ⁻ | 3 | 7 | – | – | 1341.1 |
| 1372 | [Ru ₈ (CO) ₂₀] ⁻ | 10 | – | – | – | 1369.1 |
| 1400 | [Ru ₈ (CO) ₂₁] ⁻ | 5 | – | – | – | 1397.1 |
| 1361 | [Ru ₉ (CO) ₁₆] ⁻ | – | 10 | ^a | ^a | 1359.0 |
| 1386 | [Ru ₉ (CO) ₁₇] ⁻ | – | 8 | ^a | ^a | 1387.0 |
| 1413 | [Ru ₉ (CO) ₁₈] ⁻ | – | 9 | ^a | ^a | 1415.0 |
| 1442 | [Ru ₉ (CO) ₁₉] ⁻ | 2 | 8 | ^a | ^a | 1443.0 |
| 1470 | [Ru ₉ (CO) ₂₀] ⁻ | 4 | ^a | ^a | ^a | 1471.0 |
| 1498 | [Ru ₉ (CO) ₂₁] ⁻ | 2 | ^a | ^a | ^a | 1499.0 |
| 1526 | [Ru ₉ (CO) ₂₂] ⁻ | 7 | ^a | ^a | ^a | 1527.0 |
| 1561 | [Ru ₉ (CO) ₂₃] ⁻ | 3 | ^a | ^a | ^a | 1555.0 |

^a Not assigned due to overlap of peaks.



Scheme 1.

ters, because in the absence of ligands the best way for the cluster to regain some degree of electronic saturation is to form metal–metal bonds.

All peak assignments are listed in Table 1. Considerable overlap of some of the peaks occurs, especially for the spectra of compounds **2–4**. Gas-phase aggregation may extend out as far as Ru_{10} for clusters **3** and **4** but overlap of peaks complicates their assignment in the high mass region. The most intense peak in each spectrum corresponds to $[\text{Ru}_6(\text{CO})_{17}]^-$ for **1**, $[\text{Ru}_4(\text{CO})_{12}]^-$ for **2**, $[\text{Ru}_6(\text{CO})_{12}]^-$ for **3** and $[\text{Ru}_7(\text{CO})_{14}]^-$ for **4**. Peaks which correspond to mono- or dinuclear fragments are not observed, nor does there appear to be any obvious preference overall for any particular nuclearity. These observations suggest that if charged mono- or dinuclear fragments are formed they must react very rapidly with neutral species to generate the large cluster ions seen in the mass spectra.

In summary, the decreased thermal stability of the triphenylphosphine-substituted clusters **2–4** is reflected in the gas phase reactions observed in the spectrometer. All the triphenylphosphine ligands are stripped from the clusters as well as further carbonyl ligands, generating highly unsaturated cluster fragments. These fragments aggregate to form larger clus-

ter species containing four to nine ruthenium atoms. These preliminary studies suggest that substitution of carbonyl ligands for triphenylphosphine leads to enhanced gas-phase reactivity of neutral transition metal clusters.

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