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HPLC studies of $Os_3(CO)_{12-n}(CH_3CN)_n$ ($n = 0, 1, 2$)

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Abstract

Normal and reverse phase chromatographic separation of $Os_3(CO)_{12}$, $Os_3(CO)_{11}(CH_3CN)$ and $Os_3(CO)_{10}(CH_3CN)_2$ have been examined. On a silica column good separation of these clusters can be achieved with CH_2Cl_2/petroleum ether as the mobile phase but better reproducibility is attained with a Hypersil ODS C_{18} column and a mobile phase of $MeOH/CH_3CN$. The relative retention times correlate qualitatively with molecular structures. The identities and purities of the chromatographic peaks were determined by use of a Data Evaluation Pack.

Introduction

In recent years rapid advances in high-performance liquid chromatographic technique have made it an attractive method for the separation and characterisation of mixtures of transition organometallic derivatives. Moreover this technique has also been used to monitor the formation of various organometallic complexes. Thus HPLC was employed for separation and monitoring of the reactions of non-acarbonyldiiron $Fe_2(CO)_9$ with di-t-butylsulfurdiimine [1] and the formation of binuclear carbonyl ruthenium complexes from the reaction of $Ru_3(CO)_{12}$ with 1,4-diazabutadiene [2]. Recently, separation of several trinuclear clusters of iron, ruthenium and osmium on a reverse phase column was reported by Mangia et al. [3]. Many interesting applications of the HPLC technique to organometallic compounds have been reviewed [4].

As part of our systematic studies of the separation and characterisation of transition metal clusters of osmium [5], ruthenium and iron using the HPLC technique, we report below: (a) the chromatographic behaviour of $Os_3(CO)_{12}$ (I), $Os_3(CO)_{11}(CH_3CN)$ (II) and $Os_3(CO)_{10}(CH_3CN)_2$ (III) in both normal phase and reverse phase separation and (b) the results of a study in which the identity and hence purity of narrowly spaced chromatographic peaks are established unequivocally from an examination of the relevant electronic absorption spectra.

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Results and discussion

Complete separation of the three compounds I, II, and III, was achieved in normal phase separation in which a mobile phase of 22% dichloromethane and 78% petroleum ether (40–60 °C) was used (See Fig. 1). In the reverse phase separation the best resolution was attained with a mobile phase of 55% acetonitrile and 45% methanol at a slow flow rate of 0.15 ml/min and a temperature of 35 °C (See Fig. 2). It was found that owing to the small differences in retention times of the three

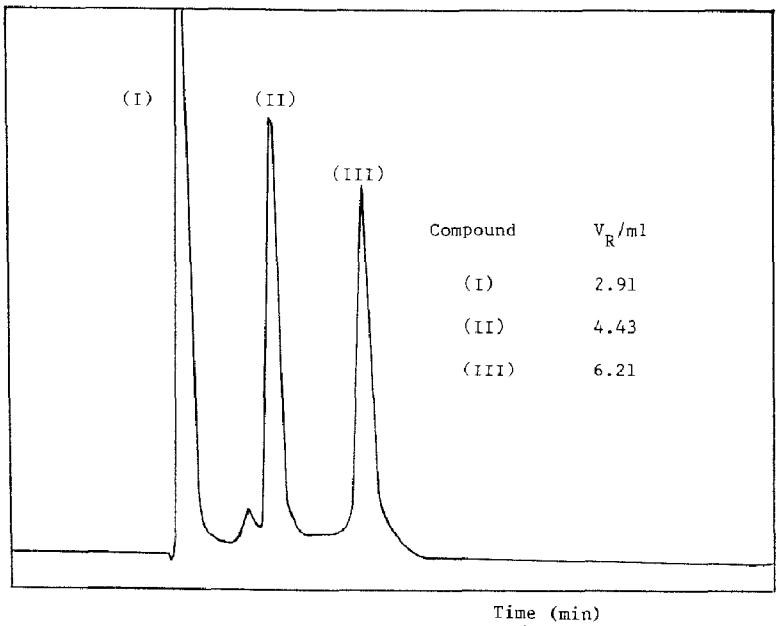

Fig. 1. Normal phase HPLC chromatogram of I, II and III. Mobile phase: 22% dicloromethane + 78% petroleum ether; column: Silica Si-100; 250 × 4.6 mm; detector wavelength: 254 nm; temperature: ambient; flowrate: 1.6 ml/min for 2.5 min; linear gradient over 1.5 min to 2.3 ml/min.

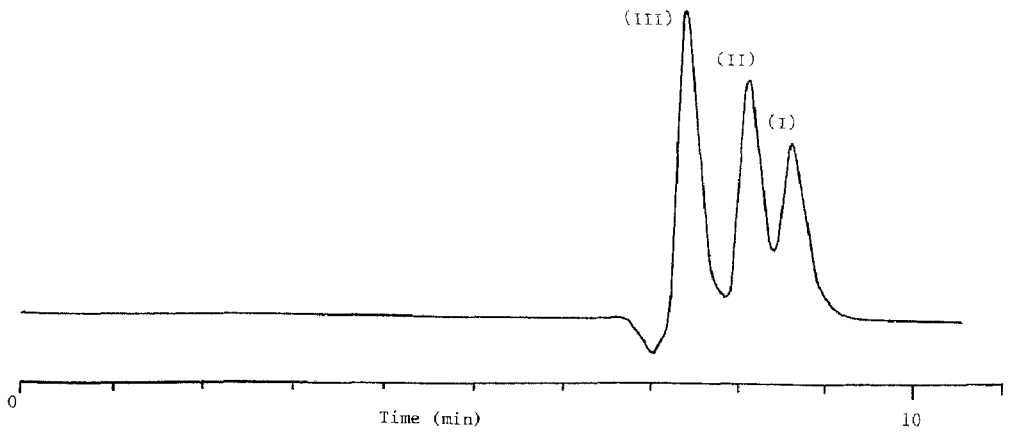

Fig. 2. Reverse phase HPLC chromatogram of I, II and III. Mobile phase Hypersil ODS C_{18}; 100 × 4.6 min; 5 μm; detector Wavelength: 254 nm; temperature: 35 °C; flow rate: 0.15 ml/min.

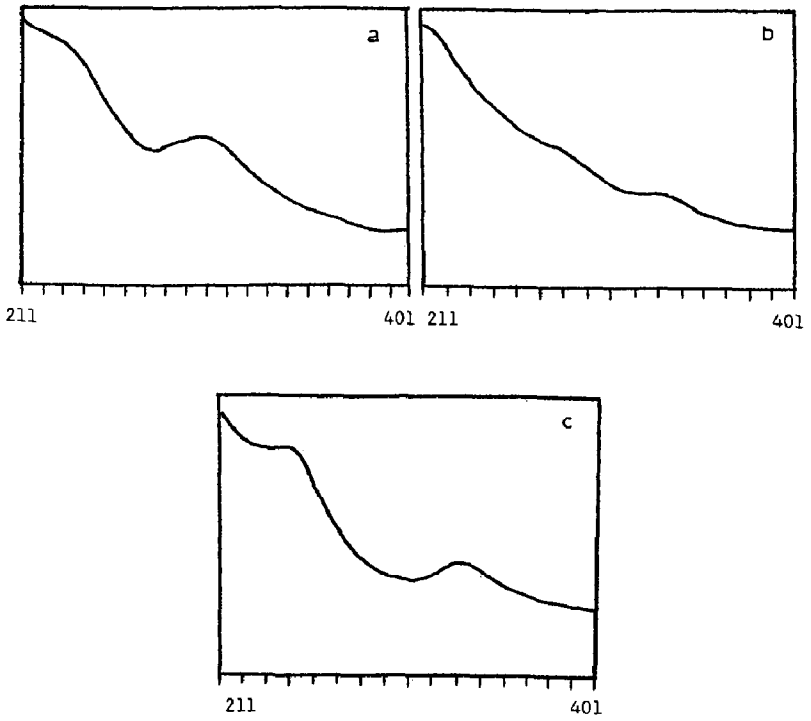

Fig. 3. UV absorption spectra (200–400 nm) between time interval (a) 7.46–7.87 min), (b) 8.17–8.42 and (c) 8.67–9.28 min. These were obtained using the photodiode array detector on HP 1090.

osmium clusters on the C_{18} column, the resolution was extremely sensitive to any variations in mobile phase composition, flow rates, and temperature.

The elution order in the normal phase is in agreement with their relative polarities [9]. Thus compound I being the most symmetrical in structure is the least polar and is eluted first, followed by compounds II and III in decreasing order of polarity. The elution order on going from normal phase to reverse phase separation is often reversed and this was found to be the case in the present study. The retention volumes thus evaluated are 2.91, 4.43, 6.21 in normal phase and 1.34, 1.25, 1.12 in reverse phase for compounds I, II, and III, respectively.

Small differences in retention times of the three osmium clusters I, II and III on a C_{18} column such as we observed were also reported by others for several other related systems [3]. Moreover, it has often been assumed that the relative retention time of each component remains unchanged in going from the pure sample to the mixture. In an effort to establish unequivocally the identity of each of the three chromatographic peaks which resulted from elution of the C_{18} column, the absorption spectra of the eluants at specified time intervals were determined by the use of the photodiode array detector and an evaluation programme of the software Data Evaluation Pack 1 for the HP85 computer. The spectra corresponding to time intervals 7.46–7.87, 8.17–8.42 and 8.67–9.28 minutes are shown in Fig. 3. These resemble closely those of $Os_3(CO)_{10}(CH_3CN)_2$, $Os_3(CO)_{11}(CH_3CN)$, and $Os_3(CO)_{12}$ (See Fig. 4) which were obtained separately with a Perkin–Elmer λ 9 spectrophotometer equipped with the PECSS software.

The Data Evaluation Pack 1 also allows for verification of the identities of the observed chromatographic peaks through determination of the ratios of the heights

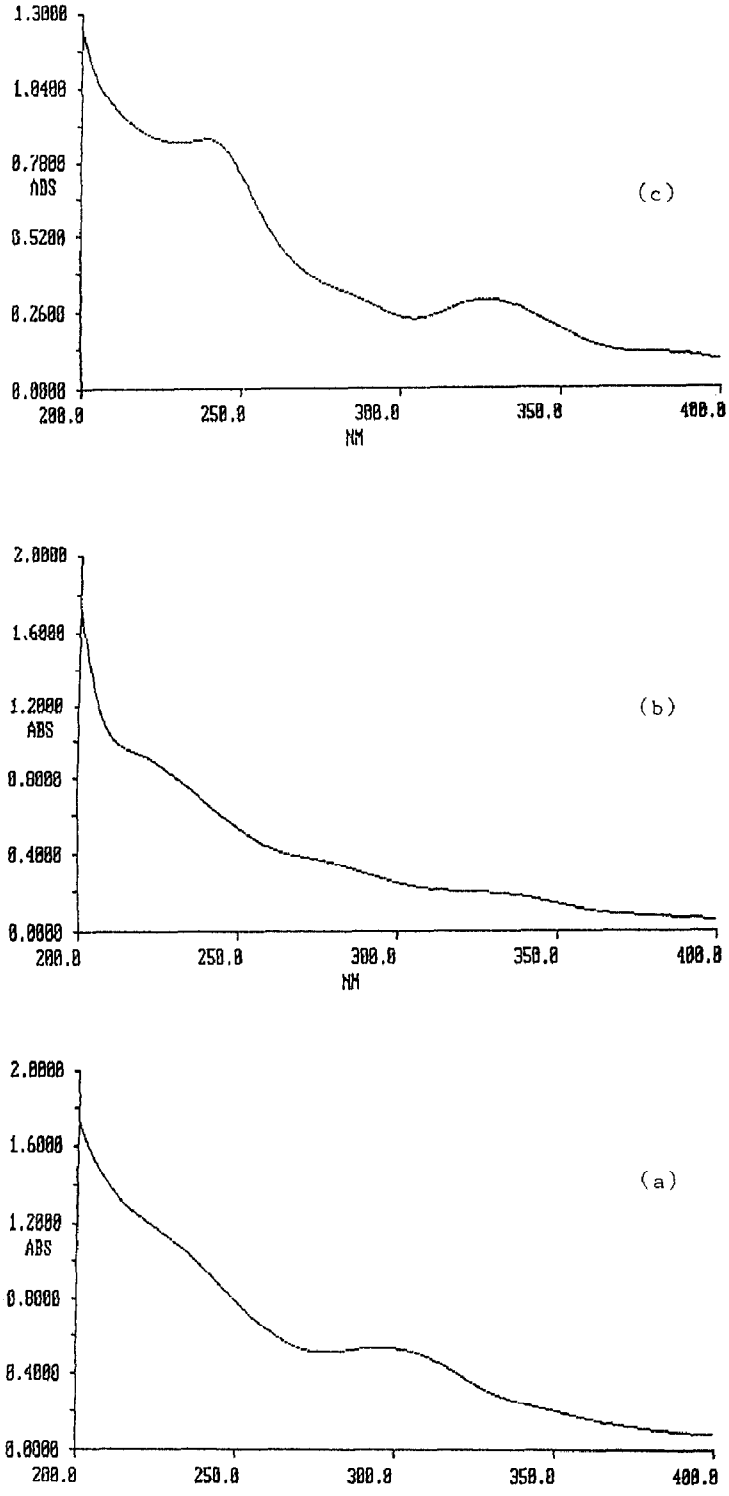

Fig. 4. UV absorption spectra (200–400 nm) of (a) $Os_3(CO)_{10}(CH_3CN)_2$, (b) $Os_3(CO)_{11}(CH_3CN)$ and (c) $Os_3(CO)_{12}$ on Perkin–Elmer λ 9 spectrophotometer.

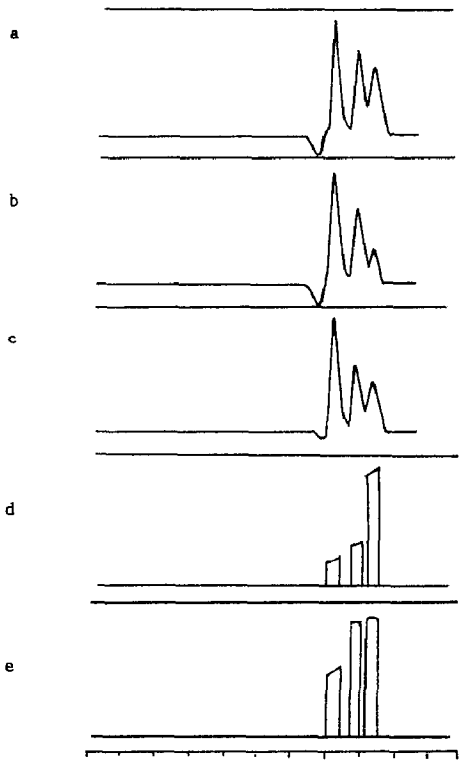

Fig. 5. Reverse phase HPLC chromatograms of I, II and III as monitored at (a) 254, (b) 290 and (c) 320 nm. (d) and (e) are ratio plots of signals at 254 mm to that at 290 nm and at 254 nm to 320 nm, respectively.

of the chromatographic peaks monitored at two or more wavelengths. If the ratio of the two signals across a peak elution profile is constant then the peak is pure. Figure 5 is a plot of the ratios of the chromatographic peaks in the reverse phase separation with signals being monitored at 320, 275, 290 nm (corresponding to absorption maxima for $Os_3(CO)_{12}$, $Os_3(CO)_{11}(CH_3CN)$ and $Os_3(CO)_{10}(CH_3CN)_2$ and at 254 m (reference signal). It seems clear that each chromatographic peak corresponds largely to a single osmium cluster.

It is envisaged that the purity checks of chromatographic peaks as demonstrated above for the reverse phase separation of $Os_3(CO)_{12}$, $Os_3(CO)_{11}(CH_3CN)$ and $Os_3(CO)_{10}(CH_3CN)_2$ will be useful not only for separation of a mixture of products but also for monitoring product formation in a given reaction. This is particularly so when the various components possess relatively small differences in retention times for a selected mode of separation.

Experimental

The separation and characterisation of the osmium clusters were undertaken using (a) a Hewlett–Packard HP 1090 Liquid Chromatograph with a HP-85B Personal Computer, 3392A integrator and a 1040A Diode-array detector, and (b) a Perkin–Elmer Series 4 Liquid Chromatograph with a 3600 Data Station and an LC75 UV detector.

The column used was an HP Si-100 silica column, 10 μm, 250 $\times$ 4.6 mm diameter for normal phase analysis and a Hypersil ODS C_{18}, 5 μm, 100 $\times$ 4.6 mm diameter for reverse phase analysis. All mobile phases used were of HPLC grade. Sample sizes were as follows: 50 μl volumes of sample solutions made up from 22% dichloromethane + 78% petroleum ether were injected in normal phase analysis and 5 μl volumes of acetonitrile solution were used for reverse phase analysis.

The osmium clusters I, II and III were made by published methods [6–8]. The preparation always resulted in a mixture of both mono- and di-substituted complexes. Although stoichiometric amounts of the reactants were used, it was difficult to prevent completely the formation of the other acetonitrile complex.

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