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High performance liquid chromatography of osmium carbonyl clusters

Rajesh Khattar, Brian F.G. Johnson and Jack Lewis *

University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)

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Abstract

The use of high performance liquid chromatography as a means of separating osmium cluster compounds is described.

High performance liquid chromatography (HPLC) has found extensive applicability in organometallic chemistry. It is a powerful technique for the characterisation and separation of organometallic compounds and has a number of advantages over the conventional thin layer chromatography (TLC). One of the major advantages of separation by HPLC is the good resolution of bands with a typical retention time of 10–15 min compared to several hours by TLC. Furthermore, the recovery of the separated sample is almost quantitative. Recently, there have been a number of reports concerning the HPLC separations of a number of cationic and neutral cluster compounds [1–7]. Our research is mainly concerned with the synthesis and reactivity of osmium carbonyl clusters and in our laboratory TLC separations has been widely used for their purification and isolation, which is a very time consuming technique and does not necessarily lead to the isolation of products in the purest form. Particularly, the clusters such as $Os_5C(CO)_{15}$, $Os_5(CO)_{16}$, $Os_7(CO)_{21}$, $Os_8C(CO)_{21}$ and $Os_8(CO)_{23}$ which are obtained in about 5–10% yields from the vacuum pyrolysis of $Os_3(CO)_{12}$, [8] their separation by TLC is not quantitative. Furthermore, due to the very similar R_f values, the bands run so close to each other on the plate that their isolation in the purest form is almost impossible. We have recently found that this problem can be overcome by the use of HPLC and within a matter of minutes the separation of all these clusters can be achieved in the purest forms. In this paper we wish to report the applicability of this technique to the binary carbonyl clusters of osmium and some of the acetonitrile substituted Os_6 clusters.

Experimental

The clusters $Os_5C(CO)_{15}$, $Os_5(CO)_{16}$, $Os_6(CO)_{18}$, $Os_7(CO)_{21}$, $Os_8C(CO)_{21}$ and $Os_8(CO)_{23}$ were obtained as a mixture of products from the vacuum pyrolysis of

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$Os_3(CO)_{12}$ [8]. The acetonitrile derivatives $Os_6(CO)_{20}(NCMe)$ and $Os_6(CO)_{19}(NCMe)_2$ were prepared by methods previously reported [9].

The HPLC separations were performed using a Gilson liquid chromatograph model 1303, equipped with a Rheodyne injection valve and a variable-wavelength holochrome UV-visible detector. Columns: Analytical column Dynamax Si Scout, 10 μm (260 × 4.6 mm) obtained from Rainin Instruments Co, Inc.; Guard Column: Li Chroprep Si-60. Preparative column: Dynamax Macro HPLC Si, 8 μm (250 × 22 mm) obtained from Rainin Instruments Co, Inc.; Guard column: Dynamax Guard Si, 8 μm (100 × 22 mm). Solvents were HPLC grade, filtered and degassed prior to use. Isocratic separations were performed on a analytical column with a flow rate of 1 ml/min and on preprative column with a flow rate of 20 ml/min. The pyrolysis mixture was initially filtered through silica to remove any anionic clusters and 2.0 ml volumes of CH_2Cl_2 solutions of the mixture were injected on a preprative column. For analytical column, 20 μl volumes were injected. The eluent used was 20% CH_2Cl_2 in hexane. The acetonitrile complexes $Os_6(CO)_{21-n}(NCMe)_n$ (where $n = 1$ or 2) which are somehow unstable in CH_2Cl_2, were dissolved in neat acetonitrile and 2.0 ml volumes were injected on a preparative column and eluted isocratically with a mixture of 70% hexane, 25% EtOAc and 5% MeCN. For analytical column, 20 μl volumes were used. The compounds were monitored by a UV detector at 254 nm.

Results and discussion

Pyrolysis mixture

The vacuum pyrolysis [8] of $Os_3(CO)_{12}$ at 260 °C for 60 h produces a brownish-black mixture containing osmium carbonyl clusters with different nuclearities (e.g. 3, 4, 5, 6, etc.). The major product of the pyrolysis is a hexanuclear cluster, $Os_6(CO)_{18}$, which can be crystallised out and the remaining mixture was separated by TLC. For TLC separations, a mixture of ethyl acetate/cyclohexane (1/99) was initially used as an eluant. A slightly better resolution can be achieved if CH_2Cl_2/hexane (3/7) mixture is used as an eluant. As the latter mixture of solvents give good resolution on the silica gel TLC plate, it was therefore decided to use this particular combination of solvents for HPLC. Analytical silica column was intially used to study the behavior of these clusters on HPLC. The pyrolysis mixture was dissolved in CH_2Cl_2 and introduced on an analytical silica column. Different mixture of CH_2Cl_2/hexane solutions were tried and the best resolution was achieved when 20% CH_2Cl_2 in hexane was used as an eluant with a flow rate of 1 ml/min. On the preparative column, a flow rate of 20 ml/min was used to achieve a similar resolution. The chromatogram of the pyrolysis mixture is shown in Fig. 1. As can be seen from the chromatogram that within 13 min all the clusters can be separated. The different fractions were collected and characterised by comparing the carbonyl stretching frequencies in their IR spectrum. The first peak with a retention time of 5.3 min was characterised by IR to be $Os_3(CO)_{12}$, the second peak with a retention time of 6.3 min was characterised to be $Os_5(CO)_{16}$ and so on. It has been noticed that the clusters with low molecular weights travel faster on a column than with high molecular weights. In the case of $Os_5(CO)_{16}$ and $Os_5C(CO)_{15}$, the latter cluster has molecular weight lower than the former and in spite of that, the latter cluster elutes slower than the former. The retention of $Os_5C(CO)_{15}$ compared to

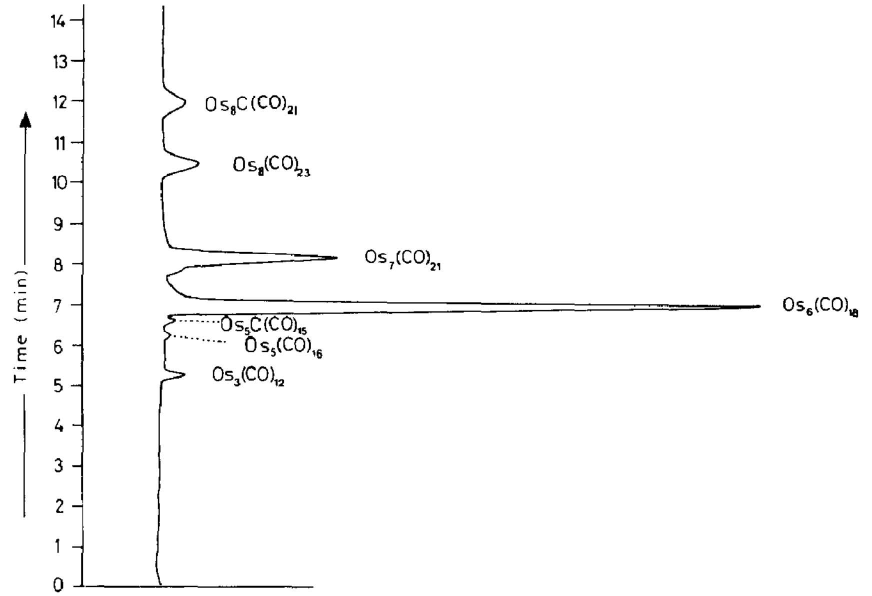

Fig. 1. Chromatogram of the $Os_3(CO)_{12}$ pyrolysis mixture. Eluent used: 20% CH_2Cl_2 in hexane.

$Os_5(CO)_{16}$ is due to the strong absorptive properties on silica. A similar trend has been observed on a silica TLC plate where the non-carbido cluster $Os_5(CO)_{16}$ with a higher molecular weight moves faster than the carbido cluster $Os_5C(CO)_{15}$ with a low molecular weight. A similar behavior has been observed in the case of $Os_8(CO)_{23}$ and $Os_8C(CO)_{21}$.

The capacity factor k' was calculated by using the relation, $k' = (t_R - t_M)/t_M$, where t_M is the retention time of the mobile phase and is recorded in Table 1. Theoretical plate numbers were calculated from $N_{theor.} = 16[t_R/W]^2$, where t_R is the retention time of the peak and W is the base width of the peak measured in the same unit (min) and is obtained by extrapolation of tangents at the points of inflection to the baseline (Table 1). The plate number of a column is a measure of the amount of spreading of a solute band as it moves down the column and efficient systems are characterised by high values of N.

Table 1

Chromatographic data for osmium carbonyl clusters

Cluster	t_R (min)	k'	$N_{theor.}$
$Os_3(CO)_{12}$	5.3	0.51	19975
$Os_5(CO)_{16}$	6.3	0.80	28224
$Os_5C(CO)_{15}$	6.7	0.91	31921
$Os_6(CO)_{18}$	7.1	1.03	5041
$Os_7(CO)_{21}$	8.2	1.34	6724
$Os_8(CO)_{23}$	10.5	2.0	4900
$Os_8C(CO)_{21}$	12.0	2.43	9216
$Os_6(CO)_{20}(NCMe)$	6.1	0.56	6615
$Os_6(CO)_{19}(NCMe)_2$	7.7	0.97	42161

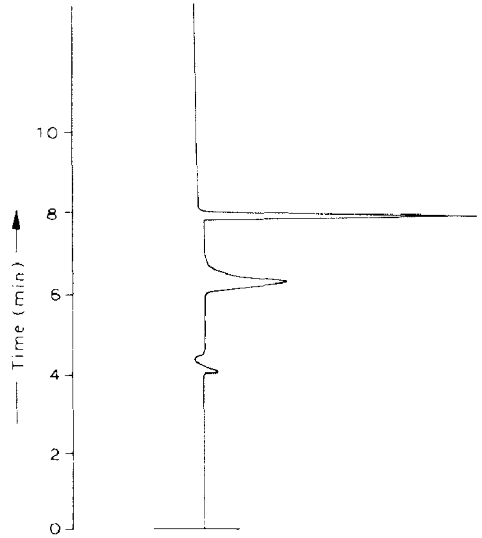

Fig. 2. Chromatogram of the acetonitrile-Os_6-raft like clusters. Eluent used: 70% hexane, 25% EtOAc, 5% MeCN.

Separation of $Os_6(CO)_{21-n}(NCMe)_n$ ($n = 1$ or 2)

Due to the presence of labile acetonitrile ligands, the complexes $Os_6(CO)_{21-n}(NCMe)_n$ ($n = 1$ or 2) are very reactive and decompose on prolonged standing in solutions (CH_2Cl_2), however, it has been noticed that these clusters show significant stability in neat acetonitrile. Initially, thin layer chromatographic technique was employed for their separation. The eluent used was 75% CCl_4, 20% $CHCl_3$, 5% MeCN. These clusters smears very badly on the TLC plate and it was not possible to isolate these species in the pure form. We have found that these two clusters can be very easily separated within a matter of minutes by the use of HPLC. Analytical silica column with a flow rate of 1 ml/min was used for their separation. The best separation was achieved when 70% hexane, 25% EtOAc, 5% MeCN was used as eluant. A flow rate of 20 ml/min is required to achieve similar resolution on a preparative silica column. The crude mixture was dissolved in neat acetonitrile and loaded on a column. A chromatogram is shown in Fig. 2. It can be seen from the chromatogram that within 8 min both these clusters can be separated. The peak with retention time 6.1 min is due to $Os_6(CO)_{20}(NCMe)$ (by IR) whereas the other at 7.7 min is due to $Os_6(CO)_{19}(NCMe)_2$ (by IR). As anticipated, the complex with low polarity and molecular weight elutes first. The peak due to $Os_6(CO)_{20}(NCMe)$ is quite broad as compared to peak due to $Os_6(CO)_{19}(NCMe)_2$. Due to the broadness of the peak, the plate number is relatively low (Table 1).

Conclusion

From the above discussion, it is concluded that the HPLC is a useful technique for the separation and characterisation of cluster complexes of osmium. The acetonitrile derivatives which somehow smears on the TLC plate due to prolonged adsorption can be very easily isolated in the pure form within a matter of minutes.

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