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Note

High-performance liquid chromatography of substituted trinuclear osmium carbonyl clusters, $Os_3(CO)_{12-n}[P(C_6F_5)_3]_n$ ($n=0$, 1, 2)

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The advantages of high-performance liquid chromatography (HPLC) over thin-layer chromatography (TLC) and column chromatography (CC) for the separation and purification of organometallic compounds and metal clusters have been well recognized [1]. These include better resolution, inert separation conditons, quantitative recovery and the relatively small sample sizes required. In paricular, as an osmium carbonyl cluster reacion often yields a host of closely related products it has become desirable to establish a HPLC method that offers not only quantitative separation but also unequivocal identification of the chromatographic peaks. The latter would be especially useful in instances of incompletely resolved chromatographic peaks. Efforts towards these ends have led to two recent reports [2,3] on the HPLC study of various osmium carbonyl clusters.

In our laboratory, a systematic study is currently being carried out to elucidate the retention mechanism and hence identify the relevant parameters that are crucial to a satisfactory separation of substituted osmium carbonyl clusters. This paper presents the findings of a study of the normal- and reversed-phase chromatographic behaviour of several substituted phosphine clusters and compares them with those for the acetonitrile complexes of osmium reported earlier.

EXPERIMENTAL

Preparation and stabilities of samples

The preparation of $Os_3(CO)_{11}[P(C_6F_5)_3]$ (I) has been reported elsewhere [4]. $Os_3(CO)_{10}[P(C_6F_5)_2]$ (II) was prepared by heating the bisacetonitrile complex $Os_3(CO)_{10}(CH_3CN)_2$ and $(C_6F_5)_3P$ (2 equiv.) in *n*-hexane at 70°C for 1 h, and purified by TLC on silica using hexane–dichloromethane (90:10) as eluent. Its m.p. is 179–181°C. It was characterized by IR, NMR and elemental analyses. Elemental analysis (calculated values in parentheses): $Os_3(CO)_{10}[P(C_6F_5)_2]$ (II), C 29.4 (28.8), P 3.37 (3.24), F 30.0 (29.8)%. ^{19}F NMR (CD_3Cl): δ −51.4(s), −69.3(q) and −81.6(t)

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ppm (reference: trifluoroacetic acid). ^{31}P NMR (CD_3Cl): δ −90.7 ppm. IR (CH_2Cl_2): ν (CO) 2107s, 2056vs, 2042vs, 2024vs, 1992s and 1983s. The clusters $Os_3(CO)_{12}$ (III). $Os_3(CO)_{11}(CH_3CN)$ (IV) and $Os_3(CO)_{10}(CH_3CN)_2$ (V) were prepared according to literature methods [5–7].

The chromatogram of each compound was determined in order to establish that the sample contained only a single component in each instance. Further, the stabilities of I–V in methanol, acetonitrile, *n*-hexane and dichloromethane were checked by monitoring the solution UV spectra of these compounds in the respective solvents. No apparent decomposition was detected up to 8 h. All chromatographic runs were made using freshly prepared solutions, however.

Instrumental method

HPLC separations were done on a Hewlett-Packard HP 1090 liquid chromatograph equipped with a Model 1040A diode-array detector, an HP 85B personal computer and a Model 3392A integrator.

The columns used were HP-100, 10 μm (250 × 4.6 mm I.D.) for normal-phase analysis and LiChrospher 100 CH-18/2, 5 μm (250 × 4 mm I.D.) for reversed-phase analysis. The mobile phases were dichloromethane–*n*-hexane (5:95) at a flow-rate of 1.0 ml/min and acetonitrile–methanol (55:45) at a flow-rate of 0.5 ml/min for normal- and reversed-phase separations respectively. The temperature in all the runs was 35°C.

All solvents were of HPLC grade and were filtered and degassed in helium prior to use. Samples were dissolved in premixed mobile phases filtered through a 0.45-μm pore filter and injected in 5-μl volumes with a Rheodyne Model 7010 injector.

The column dead volume was determined using *n*-hexane for the silica column with dichloromethane as mobile phase. For the C_{18} column, this was determined with reference to the first baseline peak which appeared on injection [8].

All retention times and volumes were corrected for dead volumes due to connecting tubings.

RESULTS AND DISCUSSION

Figs. 1 and 2 show chromatograms of the osmium clusters. Good baseline

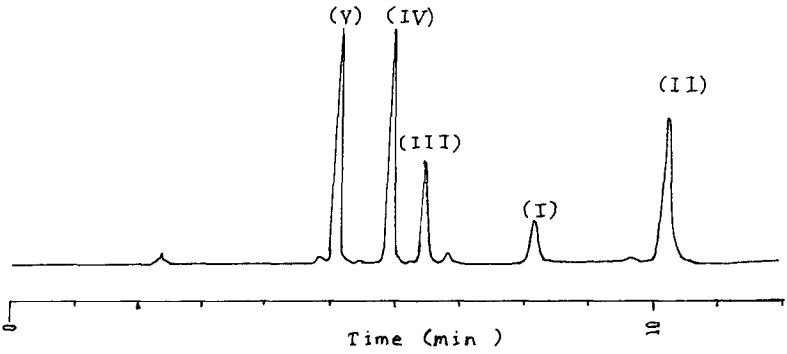

Fig. 1. Separation of $Os_3(CO)_{11}[P(C_6F_5)_3]$ (I), $Os_3(CO)_{10}[P(C_6F_5)_3]_2$ (II), $Os_3(CO)_{12}$ (III), $Os(CO)_{11}$-(CH_3CN) (IV) and $Os_3(CO)_{10}(CH_3CN)_2$ (V) on a LiChrosorb 100 CH-18/2 column. Mobile phase, acetonitrile–methanol (55:45); detection, UV (254 nm).

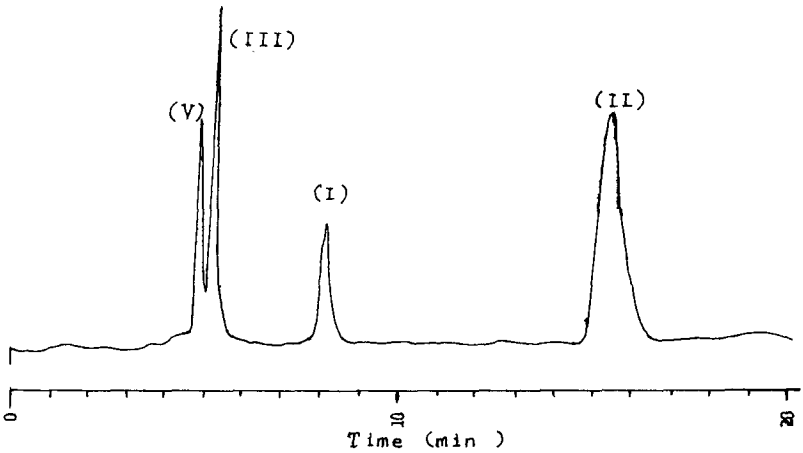

Fig. 2. Separation of $Os_3(CO)_{11}[P(C_6F_5)_3]$ (I), $Os_3(CO)_{10}[P(C_6F_5)_3]_2$ (II), $Os_3(CO)_{12}$ (III) and $Os_3(CO)_{10}(CH_3CN)_2$ (V) on an HP silica-100 column. Mobile phase, dichloromethane–*n*-hexane (5:95); flow-rate, 1.0 $cm^3\ min^{-1}$; detection, UV (230 nm).

separation was observed for all five compounds I–V on the C_{18} column with the mobile phase employed. For the normal-phase separation, chromatographic peaks due to I, II, V, III (or IV) are well resolved. Over a range of mobile phases with various proportions of dichloromethane in *n*-hexane, III and IV eluted at nearly the same time in each instance.

The capacity factor k' and the theoretical plate number N were evaluated for all chromatographic peaks in reversed- and normal-phase separations (Table I) [9]. The k' values fall into the optimum range of $0.5 < k' < 5$.

The N values of 58 000–76 000 in the reversed-phase separation are comparable to the expected value of 80 000 for a column of the given specifications. Those in the normal-phase separation, in the range 11 000–13 000 are low in comparison with the values evaluated using standard equations for a well packed column of the given specifications [9]. However, for most practical applications these values are acceptable [10].

The elution order of I, II and III on the reversed-phase column is such that the retention volumes increase with increasing number of phenyl groups resulting in III being eluted first followed by I and then II. The retardation of clusters containing triarylphosphine ligands has been reported for both reversed- and normal-phase separations of a series of derivatives of the tetranuclear clusters $(Cp)NiOs_3(\mu\text{-}H)_3(CO)_8L$ [11–13] [Cp = cyclopentadienyl; L = CO, PPh_2H, Ph_3 and $P(o\text{-tolyl})_3$]. The differences in retention volumes of that series of compounds were correlated with the different degrees of steric hindrance with the derivative containing the largest aryl group (tris-tolyl) being eluted last. For the clusters III, IV and V, their relative solubilities in the mobile phase appear to be the dominant factor. Thus V has the highest solubility and is eluted first, followed by IV and finally III. Current theories on the retention mechanism of chemically bonded phases [14–16] are in support of these correlations.

TABLE I

CAPACITY FACTORS (k') AND NUMBER OF THEORETICAL PLATES (N) UNDER (A) REVERSED-PHASE AND (B) NORMAL-PHASE CONDITIONS

Parameter	$Os_3(CO)_{10}(CH_3CN)_2$		$Os_3(CO)_{11}(CH_3CN)$		$Os_3(CO)_{12}$		$Os_3(CO)_{11}P(C_6F_5)_3$		$Os_3(CO)_{10}[P(C_6F_5)_3]_2$	
	A[a]	B[b]	A	B	A	B	A	B	A	B
k'	1.48	0.78	1.89	0.92	2.16	2.01	3.00	2.01	4.03	4.70
N (m^{-1})	58 190	11 500	68 060	13 000	72 010	12 670	75 390	12 670	76 740	12 640

[a] t_0 = 2.00.
[b] t_0 = 2.68.

Polar interactions between the silica surface and the ligands apparently determine the order of elution for the normal-phase separation. Thus the retention volumes increase with the number of substituted phosphines $[P(C_6F_5)_3]$ for I, II and III, and with the number of carbonyls for III and V. The larger differences in retention volumes among I, II and III than between III and IV are consistent with the more polar character of the $P(C_6F_5)_3$ group relative to the carbonyl which, on the other hand, is more similar to acetonitrile.

In most chromatographic studies, it has often been assumed that the relative retention time of each compound remains unchanged on going from a pure sample to a mixture. Moreover, two closely overlapped peaks may be mistaken as being due to a single component. In an effort to establish unequivocally the identity and purity of the observed chromatographic peaks, the absorption spectra of the eluates at the specified time corresponding to the peak maxima were determined using a photodiode-array detector and an evaluation program of the Data Evaluation Pack software

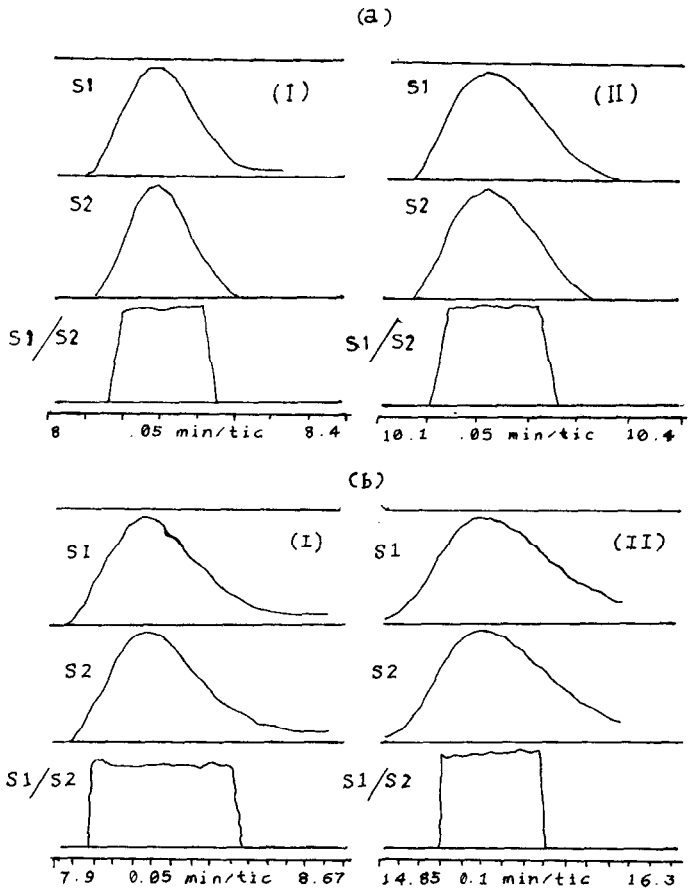

Fig. 3. Signal plots at 230 nm (S1), 254 nm (S2) and ratio plots (S1/S2) for $Os_3(CO)_{11}[P(C_6F_5)_3]$ (I) and $Os_3(CO)_{10}[P(C_6F_5)_3]_2$ (II) under (a) reversed-phase and (b) normal-phase conditions.

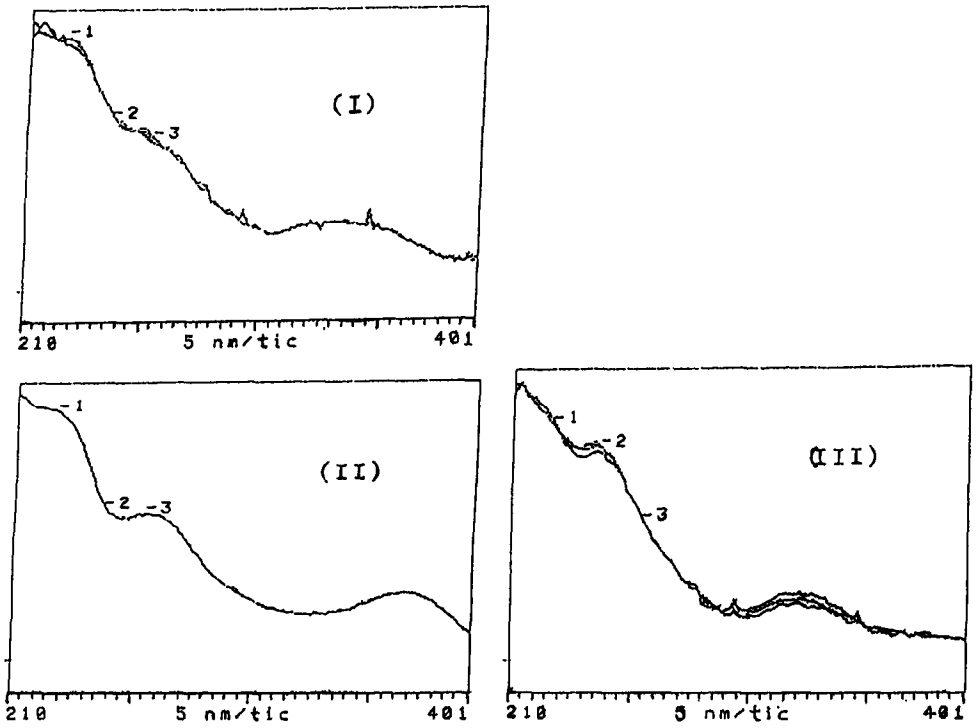

Fig. 4. Overlays of spectra at (1) upslope, (2) apex and (3) downslope for reversed-phase separation of $Os_3(CO)_{11}[P(C_6F_5)_3]$ (I) $Os_3(CO)_{10}[P(C_6F_5)_3]_2$ (II) and $Os_3(CO)_{12}$ (III).

of the HP 85B computer. Comparisons of the spectra thus obtained with the individual spectra of the five compounds which were determined separately on a Perkin-Elmer Lambda-9 spectrophotometer established unequivocally the identities of the observed chromatographic peaks as given in Figs. 1 and 2.

Further, the purity of each of the chromatographic peaks was verified through determinations of (a) the ratios of the heights of a chromatographic peak monitored at two or more wavelengths and (b) the overlay of the absorption spectra at three different points (upslope, apex and downslope) of each peak. For a pure chromatographic peak, the ratio of two signals across a peak elution profile should remain fairly constant. Some typical ratio plots and plots of spectral overlays of selected chromatographic peaks are given in Figs. 3 and 4. Using these methods, each of the chromatographic peaks in the reversed-phase separation was found to correspond to a single osmium cluster. For the normal-phase separation, peaks corresponding to I, II and V are pure whereas the peak due to the overlap of III and IV is characterized by a varying ratio plot and also an ill-matched spectral overlay.

REFERENCES

1 A. Casoli, A. Mangia and G. Predieri, *Chem. Rev.*, 89 (1989) 407.
2 R. Khattar, B. F. G. Johnson and J. Lewis, *J. Organomet. Chem.*, 334 (1988) 221.
3 H. G. Ang, W. L. Kwik and W. K. Leong, *J. Organomet. Chem.*, 379 (1989) 325.
4 H. G. Ang, W. L. Kwik and W. K. Leong, *Acta Crystallogr.*, Sect. C, 45 (1989) 1713.
5 B. F. G. Johnson, J. Lewis and P. A. Kilty, *J. Chem. Soc. A*, (1968) 2859.
6 B. F. G. Johnson, J. Lewis and D. Pippard, *J. Organomet. Chem.*, 145 (1978) C4.
7 M. Tachikawa and J. R. Shapley, *J. Organomet. Chem.*, 124 (1977) C19.
8 W. L. Hine, T. E. Riene, D. W. Armstrong, DeMond, A. Ala and T. Ward, *Anal. Chem.*, 57 (1985) 237.
9 L. R. Snyder, in C. Horváth (Editor), *J. High Performance Liquid Chromatography: Advances and Perspectives*, Vol. 3, Academic Press, New York, 1983, Ch. 5.
10 V. R. Meyer, *J. Chromatogr.*, 334 (1985) 197.
11 A. Casoli, A. Mangia, G. Predieri and E. Sapa, *J. Chromatogr.*, 447 (1988) 187.
12 A. Casoli, A. Mangia and G. Predieri, *Anal. Chim. Acta*, 176 (1985) 259.
13 A. Casoli, A. Mangia, G. Predieri and G. Sappa, *Anal. Chim. Acta*, 152 (1984) 289.
14 K. A. Dill, *J. Phys. Chem.*, 91 (1987) 1980.
15 D. E. Martire and R. E. Boehm, *J. Phys. Chem.*, 87 (1983) 1045.
16 P. T. Ying, J. G. Dorsey and K. A. Dill, *Anal. Chem.*, 61 (1989) 2540.