Journal of Fluorine Chemistry, 51 (1991) 83–91

Received: June 12, 1990; accepted: August 17, 1990

SYNTHETIC, SPECTROSCOPIC AND HPLC STUDIES OF SOME SUBSTITUTED OSMIUM CLUSTERS CONTAINING PENTAFLUOROBENZOATE LIGAND

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SUMMARY

Reactions of pentafluorobenzoic acid with $Os_3(CO)_{10}(CH_3CN)_2$ and $Os_3(CO)_{11}(CH_3CN)$ afforded two new carboxylate triosmium carbonyl clusters viz. $Os_3(CO)_{10}H(\mu-C_6F_5CO_2)$ and $Os_3(CO)_{11}H(C_6F_5CO_2)$ respectively. I.r. and ^{1}H n.m.r. spectral data suggest that the pentafluorobenzoate acts as a bridging ligand in one case and as a unidentate ligand in the other.

INTRODUCTION

Dodecacarbonyltriosmium has been reported to react with several carboxylic acids (RCOOH, R=H, Me or Et) to give dimeric complexes of the type $[Os(CO)_2(RCO_2)]_2$ [1]. On the other hand, substituted triosmium carbonyls containing a good leaving group such as n-cyclohexa-1, 3-diene in $Os_3(CO)_{10}(C_6H_8)$ [2] and cyclooctene in $Os_3(CO)_{10}(C_8H_{14})$ [3], were found to react with carboxylic acids (RCOOH, R=H, Me, Et, Ph, CF_3) to afford trinuclear osmium carbonyl clusters of the general formula $Os_3(CO)_{10}H(O_2CR)$ [2,3]. The i.r and nmr spectral data indicated that the carboxylate ligand in each of these clusters bridged across two osmium atoms. An X-ray analysis of the formate

0022-1139/91/$3.50

compound $(\mu\text{-H})(\mu\text{-O}_2\text{CH})\text{Os}_3(\text{CO})_{10}$ showed that the carboxylate ligand in fact bridged diaxially across two osmium atoms which were also bridged by the hydride ligand diequatorially. In addition, osmium clusters of higher nuclearity containing bridging trifluoroacetate ligands have recently been reported [3]. However, no example of triosmium carbonyl cluster containing a unidentate carboxylate ligand has been reported.

We report here the isolation and characterisation of two new carboxylate triosmium carbonyl complexes $\text{Os}_3(\text{CO})_{10}\text{H}(\mu\text{-C}_6\text{F}_5\text{CO}_2)$ and $\text{Os}_3(\text{CO})_{11}\text{H}(\text{C}_6\text{F}_5\text{CO}_2)$ from reactions of pentafluorobenzoic acid with (a) $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ (I) and (b) $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ (II) respectively. The high performance liquid chromatographic study of these complexes will also be described.

RESULTS AND DISCUSSION

Synthetic and Spectroscopic Study

Pentafluorobenzoic acid reacts with $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ (I) and $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ (II) in dichloromethane at 60 °C to give $\text{Os}_3(\text{CO})_{10}\text{H}(\mu\text{-C}_6\text{F}_5\text{CO}_2)$ (III) and $\text{Os}_3(\text{CO})_{11}\text{H}(\text{C}_6\text{F}_5\text{CO}_2)$ (IV) respectively. The formulations of (III) and (IV) are established by elemental analyses, i.r. and $^1\text{H}/^{19}\text{F}$ nmr spectral analyses.

Table 1 lists the carbonyl stretchings of (III), (IV) and two other related compounds. It will be evident that (III) displays ν(CO) stretchings that closely resemble those of $\text{Os}_3(\text{CO})_{10}\text{H}(\text{CO}_2\text{Ph})$ [2] and markedly differ from those of (IV). On the other hand, the carbonyl stretchings of (IV) are similar to those of the substituted osmium carbonyl cluster (μ-H)$\text{Os}_3(\text{CO})_{11}\{(\text{CF}_3)_2\text{NO}\}$ [5] which has been shown from an x-ray structural analysis to contain a unidentate $(\text{CF}_3)_2\text{NO}$ at the terminal position of an osmium atom which is also bridged by a hydride ion to one of the other two osmium in the cluster.

Thus a comparison of the carbonyl stretching frequencies strongly suggests that (III) should be formulated as $\text{Os}_3(\text{CO})_{10}\text{H}(\mu$-

TABLE 1

Spectroscopic data for III and IV

	i.r. spectra [(CO)/cm^{-1}]							
III	2115w	2077s	2065s	2025s	2016s		1984m,br	
[$Os_3(CO)_{10}H(CO_2Ph)$]*	2111w	2072s	2061s	2024s	2013s		1983m	1979m
IV	2145w	2099s	2077vs	2067vs	2060vs	2034vs	2016s	1994m,br
($Os_3(CO)_{11}H(CF_3)_2NO$	2145m	2099s	2077vs	2070vs	2057s	2037s	2017s	1990m

* Recorded in cyclohexane

$C_6F_5CO_2$) and (IV) as $Os_3(CO)_{11}H(C_6F_5CO_2)$. To substantiate these formulations, the i.r. spectra (KBr) of these compounds have been carefully examined in the 1800-1300 cm^{-1} region into which the symmetric and asymmetric carboxyl stretching vibrations fall. An analysis of the three spectra due to free $C_6F_5CO_2H$, (III) and (IV) reveals that the ring and skeletal vibrations [6] due to the C_6F_5 ring can be separated from those due to the symmetric and asymmetric carboxyl stretching frequencies [7]. Upon complexation, the C-F ring and skeletal vibrations have not been significantly altered. On the other hand the ν(C=O) at 1713 cm^{-1} disappears to be replaced by two strong bands at 1578 and 1417 cm^{-1} in (III) and 1659 and 1348 cm^{-1} in (IV). These are characteristics of the asymmetric and symmetric carboxyl stretching of metal complexes. Moreover, the large $\Delta\nu$ (νasym - νsymm) of 311 cm^{-1} for (IV) is consistent with the unidentate mode of binding of $C_6F_5CO_2^-$ in this complex while a value of of 161 cm^{-1} for (III) is typical of those for bridging carboxylate [7].

The ^1H and ^{19}F n.m.r. spectra of (III) and (IV) lend further to these formulations. The chemical shifts of the hydride signal in (III) (-10.35 ppm) and (IV) (-15.27 ppm) are comparable to those of $Os_3(CO)_{10}H(\mu\text{-}C_6H_5CO_2)$ (-10.30 ppm) and $Os_3(CO)_{11}H\{(CF_3)_2NO\}$ (-14.21 ppm) respectively. Both (III) and (IV) display ^{19}F nmr spectra typical of the pentafluorophenyl ring.

HPLC Study of (I) - (V)

Figure 1 shows a typical chromatogram of a synthetic mixture of (I)-(V) on a LiChrosphere CH18/2 column using 100% MeCN as the mobile phase. The elution order of these compounds can be correlated with the relative molecular sizes and polarities. Thus compound (V) is the most symmetrical and least bulky and hence has longer retention time than (I), (II) and (IV). (IV) is the least symmetrical and most polar of the five and hence has the shortest retention time.

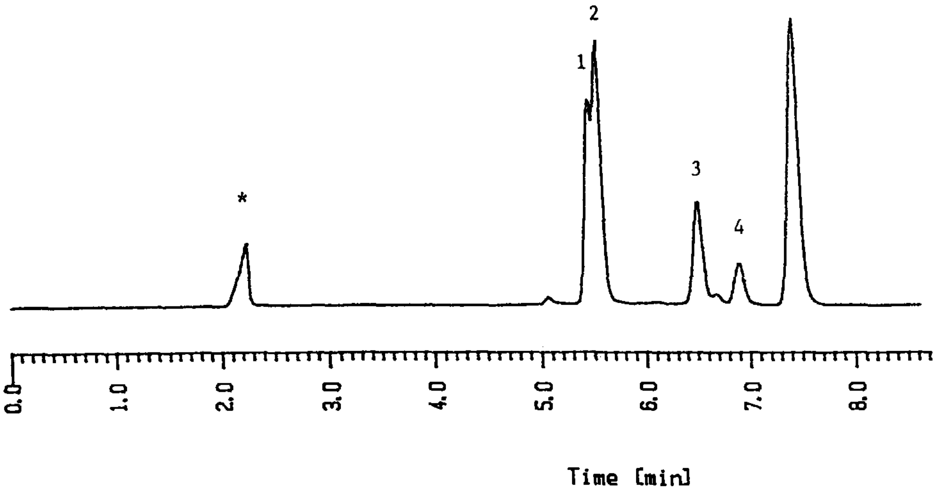


Fig.1. Reversed phase HPLC chromatogram of $Os_3(CO)_{11}H(C_6F_5CO_2)$ (1), $Os_3(CO)_{10}(NCMe)_2$(2), $Os_3(CO)_{11}(NCMe)$(3), $Os_3(CO)_{12}$(4) and $Os_3(CO)_{10}H(C_6F_5CO_2)$ (5).

Mobile phase : 95% MeCN and 5% MeOH;
Column : LiChrospher CH 18/2; 250 x 4 mm, 5um;
Detector wavelength : 254 nm; temperature : ambient;
Flowrate : 0.5 ml/min.

(* - This is the peak for pentafluorobenzoic acid)

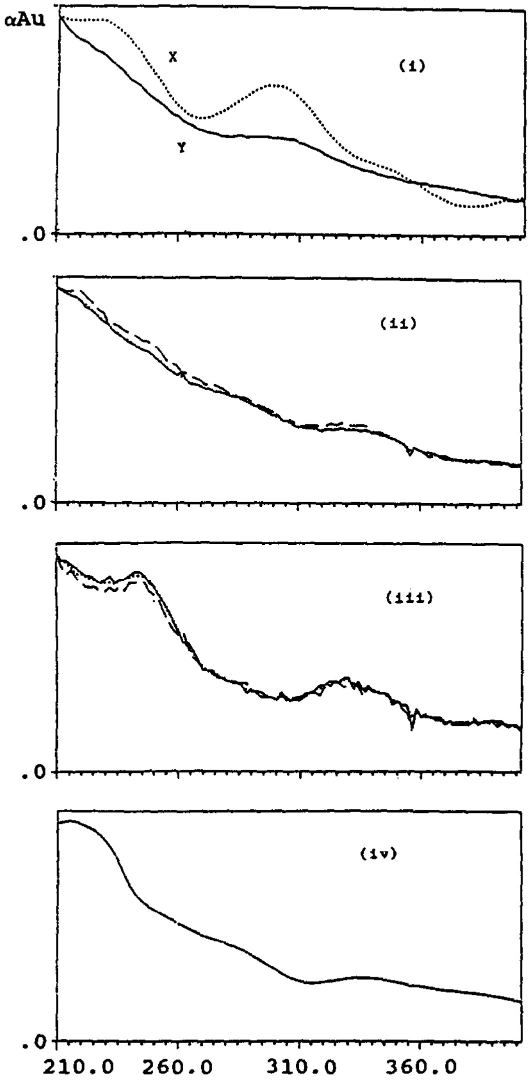
The relative purity of the peaks has been checked by overlaying the uv absorption spectra measured for a given peak at the beginning of the upslope, at the apex and at the end of the downslope. If these spectra are superimposable then the given peak is composed of one single component. As can be seen for compound (II), (III) and (V) the spectral overlays match exactly (Fig.2). For compounds (I) and (IV) the spectral plots taken at the upslope of two overlapping peaks show two different spectra (X) and (Y) which are in fact similar to those of $Os_3(CO)_{11}H(C_6F_5CO_2)$ and $Os_3(CO)_{10}(CH_3CN)_2$ respectively.

(IV) was found to be relatively unstable when MeOH was used as one of the solvents in the mobile phase. Four major peaks were detected for a sample of (IV) when a mixed solvent of 5%CH_3OH/95%CH_3CN was used as the mobile phase (Fig.3). Using the methods described above, the peaks at 2.09, 5.47, 6.57 and 6.95 min were identified to be C_6F_5COOH, (IV), (II) and (V) respectively. (IV) apparently underwent decomposition in the presence of CH_3OH to yield pentafluorobenzoic acid, $Os_3(CO)_{11}(CH_3CN)$ and $Os_3(CO)_{12}$.

EXPERIMENTAL

$Os_3(CO)_{12}$, $Os_3(CO)_{10}(CH_3CN)_2$ and $Os_3(CO)_{11}(CH_3CN)$ were prepared by literature methods [8,9]. $C_6F_5CO_2H$ was obtained from Aldrich Chemical Co. Inc. All the reactions were carried out in the absence of oxygen.

The i.r. spectra in the 4000-400 cm^{-1} region were recorded on a Perkin - Elmer 983 model. The ^1H and ^{19}F nmr spectra were obtained at 90 MHz using a Joel FX90 FT NMR spectrometer. The HPLC separations of the triosmium clusters were undertaken using a Hewlett-Packard HP1090 Liquid Chromatograph with a HP-85 personal computer, 3392-A integrator and a 1040 A diode-array detector.



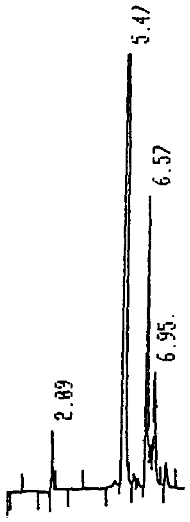


Fig.2. Spectral Overlay Plots.

(i)absorption spectra at upslope of peaks (1) and (2) and (ii),(iii),(iv) absorption spectra at upslope, apex and downslope of peaks (3), (4), (5) respectively

Fig.3. Reversed phase HPLC chromatogram of a sample containing (IV) in 95%MeCN/5%MeOH
Mobile phase : 95%MeCN + 5% MeOH
Other conditions same as in Fig.1a.

HPLC Study

It has been found that the mono- or bis- acetonitrile complexes $Os_3(CO)_{12-n}(CH_3CN)_n$ (n = 1 or 2) prepared from $Os_3(CO)_{12}$ according to literature methods [8,9] invariably contains small amounts of the bis- or mono- acetonitrile complex as well as $Os_3(CO)_{12}$ (V). In turn the products obtained from the reactions of (I) and (II) with C_6F_5COOH would have trace amounts of (IV) and (III) respectively. Complete separation by TLC of these osmium carbonyl clusters proved to be very time consuming as the TLC process had to be repeated several times. Thus a study of the HPLC separations of the five compounds (I)-(V) was undertaken. The elution order was established to be (IV), (I), (II), (V) and (III) with the chromatographic peaks being identified by both the retention times and the corresponding uv absorption spectra which were obtained using a photodiode array detector. Although peaks due to (IV)(5.45min) and (I)(5.55min) are only marginally resolved, the spectra of the eluants at the times specified are clearly those of (IV) and (I) respectively (Fig. 1).

Preparation of $Os_3(CO)_{10}H(C_6F_5CO_2)$

$Os_3(CO)_{10}(CH_3CN)_2$ (0.09 g, 9.6 x 10^{-5} mol) and $C_6F_5CO_2H$ (0.05 g, 2.36 x 10^{-4} mol) were dissolved in CH_2Cl_2 (10 ml), sealed in a Carius tube and heated to 60 °C for 16 hours. The solvent was removed in vacuo and the residue was chromatographed on thin layer silica plates using hexane - CH_2Cl_2 (9:1) as eluant. (III) was the major product and isolated as a crystalline yellow solid. Yield 0.062 g, 62%. (Analysis: Found: C, 19.7; F, 9.0%, $C_{17}HF_5O_{12}Os_3$ requires C, 19.2%; F, 8.9%). IR(cm^{-1}) (KBr) 1645w (δ C-F), 1578s (ν_a CO_2^-), 1525m and 1483s (δ C-F) and 1417m (ν_s CO_2^-). ^1H nmr ($CDCl_3$)δ= -10.35 ppm (Os - H), ^{19}F nmr ($CDCl_3$) δ= -61.89(d, J = 14.65 Hz, 2H, ortho F), -72.39(t, J = - 19.53Hz, 1F, para F) and -85.19 ppm (m, 2F, meta-F).

Preparation of $Os_3(CO)_{11}H(C_6F_5CO_2)$

$Os_3(CO)_{11}(CH_3CN)$ (0.05 g, 5.44×10^{-5} mol) and $C_6F_5CO_2H$ (0.02 g, 1.08×10^{-4} mol) were dissovled in CH_2Cl_2 (10 cm^3), sealed in a Carius tube and heated to 60 C for 24 hours. The yellow residue obtained after removal of the solvent was purified by TLC on silica plates using CH_2Cl_2 - hexane (9:1) as eluant. As for (III), (IV) was obtained as the major product in the form of a yellow solid. This was further recrystallised from CH_2Cl_2. Yield 0.03g, 52%. Analysis: Found: C, 19.83; F, 8.72%, $C_{18}HF_5O_{12}Os_3$ requires C, 20.11; F, 8.83%. IR(cm^{-1}) (KBr) 1659s ($\nu_a CO_2^-$), 1517m and 1494s (δ C-F), 1348 ($\nu_s CO_2^-$). ^1H nmr ($CDCl_3$) δ = -15.27 ppm (Os-H). ^{19}F nmr ($CDCl_3$) δ = -65.94 (d, J = 14.65 Hz, 2F, ortho F), -78.31 (m, 1F para F) and -86.18 ppm (m, 2F, meta F).

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