Journal of Fluorine Chemistry, 60 (1993) 43–48

Reaction of pentafluoronitrosobenzene with $[Os_3(CO)_{11}(CH_3CN)]$ and high-performance liquid chromatographic separation of $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$, $[Os_3(CO)_9(\mu_3\text{-}NC_6F_5)_2]$, $[Os_3(CO)_{11}(CH_3CN)]$ and $Os_3(CO)_{12}$

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(Received December 2, 1991; accepted April 14, 1992)

Abstract

Reaction of pentafluoronitrosobenzene with $[Os_3(CO)_{11}(CH_3CN)]$ in THF at room temperature yields a new triosmium cluster, $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$ (**I**), where the pentafluorophenylnitroso ligand has been shown by X-ray crystallography to adopt an unusual bonding mode, with its nitrogen bridging two non-bonded osmium atoms and the oxygen atom bonded to one of the osmium atoms. The separation of $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$ (**I**), $[Os_3(CO)_9(\mu_3\text{-}NC_6F_5)_2]$ (**II**) and their parent triosmium clusters, i.e. $[Os_3(CO)_{11}(CH_3CN)]$ and $Os_3(CO)_{12}$, by high-performance liquid chromatography is also described.

Introduction

We have previously reported the reaction of pentafluoronitrosobenzene with $Os_3(CO)_{12}$ [1] which afforded a bis(pentafluorophenylimido) cluster characterized as $[Os_3(CO)_9(\mu_3\text{-}NC_6F_5)_2]$ (**II**). As a continuation of our studies on the coordination properties of pentafluoronitrosobenzene, we now report the reaction of pentafluoronitrosobenzene with $[Os_3(CO)_{11}(CH_3CN)]$ which gives a new open cluster with the C_6F_5NO moiety remaining intact rendering it the first example of a triosmium cluster containing pentafluoronitrosobenzene.

In this paper, we also describe the high-performance liquid chromatographic separation of a mixture of $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$, $[Os_3(CO)_9(\mu_3\text{-}NC_6F_5)_2]$, $[Os_3(CO)_{11}(CH_3CN)]$ and $Os_3(CO)_{12}$ on a LiChrospher-100 RP-18 column using 10% water/90% acetonitrile as the mobile phase. The identity and purity of the chromatographic peaks were determined by a Data Evaluation Pack.

Results and discussion

Synthesis and characterization of $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$

The new cluster, $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$ (**I**) (Fig. 1), was prepared upon addition of pentafluoronitrosobenzene in THF to $[Os_3(CO)_{11}(CH_3CN)]$ dis-

0022-1139/93/$6.00

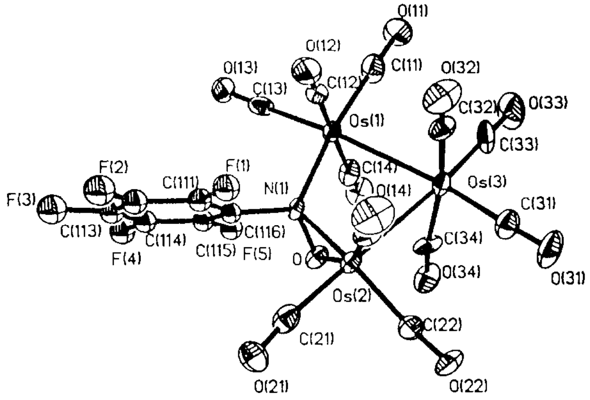

Fig. 1. An ORTEP drawing of $Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)$.

solved in THF at room temperature in a nitrogen atmosphere. The infrared spectrum of **I** exhibits carbonyl stretching frequencies at 2134(m), 2113(w), 2106(w), 2087(vs), 2075(m), 2062(vs), 2057(vs), 2052(vs), 2041(m), 2030(sh), 2024(vs), 2006(vs), 1997(s), 1982(s) and 1976(sh) cm^{-1}. The doublet at 1513 cm^{-1} is attributed to the pentafluorophenyl ring vibration [2] and the band at 1006 cm^{-1} is probably due to N—O stretching [3]. Three sets of signals characteristic of pentafluorophenyl ring resonance are observed in the ^{19}F NMR spectrum in $CDCl_3$ at $\delta -67.94$ (m, 2F), -81.26 (m, 1F) and -84.90 (m, 2F) ppm with respect to TFA.

The molecular structure of **I** was determined by a single-crystal X-ray diffraction study and is shown in Fig. 1. Atomic coordinates and selected bond distances and angles are given in Tables 1 and 2, respectively. The molecular structure comprises three osmium atoms, a pentafluorophenylnitroso bridge and 11 terminally-bonded carbon monoxide ligands. In addition, the crystal exhibits a unique triangle with N, O and one of the Os atoms forming the vertices. The two-electron donor (CH_3CN) is displaced by the pentafluoronitrobenzene which acts as a four-electron donor and the cluster is open with a long Os(1)—Os(2) non-bonded distance of *c.* 3.59 Å. The Os(1)—Os(3) [2.917 Å] and Os(2)—Os(3) [2.888 Å] bond lengths fall within the range of Os—Os bond distances observed. The bond lengths of Os(1)—N(1) [2.134 Å] and Os(2)—N(1) [2.084 Å] can be compared with the average Os—N bond length [2.12 Å] in $[Os_3(CO)_9(\mu_3\text{-}NC_6F_5)_2]$ (**II**) and the Pt—N bond distance [2.084 Å] in $[Pt(PPh_3)_2(C_6H_5NO)]$ [4]. The N(1)—O bond of 1.438 Å is longer than the corresponding bond in $[Pt(PPh_3)_2(C_6H_5NO)]$ [1.410 Å] and is indicative of predominant single-bond character. The Os(1)—N(1)—C(116) and Os(2)—N(1)—C(116) bond angles were found to be 117.9° and 120.3° and the pentafluorophenyl ring is essentially planar.

Separation by high-performance liquid chromatography (HPLC)

HPLC separation of four triosmium clusters, namely $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$ (**I**), $[Os_3(CO)_9(\mu_3\text{-}NC_6F_5)_2]$ (**II**), $[Os_3(CO)_{11}(CH_3CN)]$ and $Os_3(CO)_{12}$,

TABLE 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$

	x	y	z	$U(eq)$[a]
Os(1)	4160(1)	6385(1)	3023(1)	49(1)
Os(2)	1232(1)	9751(1)	2263(1)	45(1)
Os(3)	3014(1)	9243(1)	3664(1)	52(1)
N(1)	2140(19)	7466(12)	2280(6)	38(5)
O	328(16)	7884(11)	2716(7)	49(5)
C(11)	5879(40)	5698(23)	3744(16)	90(12)
C(12)	5974(30)	7068(21)	2183(16)	63(9)
C(13)	4621(27)	4483(19)	2606(16)	69(10)
C(14)	2144(35)	5974(21)	3842(13)	65(9)
C(21)	−8(35)	10024(22)	1351(15)	73(10)
C(22)	−424(29)	11493(19)	2657(14)	65(9)
C(23)	2919(26)	10830(18)	1721(13)	56(8)
C(31)	2311(33)	11270(20)	3835(14)	73(10)
C(32)	5264(28)	9585(19)	3066(14)	60(8)
C(33)	3950(40)	8482(22)	4066(16)	83(12)
C(34)	538(22)	9021(17)	4009(16)	66(9)
O(11)	6944(27)	5300(19)	4177(11)	105(9)
O(12)	6992(23)	7434(19)	1700(12)	91(9)
O(13)	4954(24)	3360(15)	2388(11)	94(8)
O(14)	1079(26)	5699(16)	4328(11)	91(8)
O(21)	−814(27)	10374(20)	839(11)	103(9)
O(22)	−1348(19)	12488(14)	2945(10)	77(7)
O(23)	3932(25)	11399(18)	1357(13)	112(10)
O(31)	1903(26)	12474(15)	3955(12)	110(10)
O(32)	6513(25)	9889(17)	2668(14)	112(10)
O(33)	4507(35)	8080(21)	5234(13)	131(12)
O(34)	−845(22)	8990(16)	4280(10)	83(7)
C(111)	2975(27)	7017(19)	857(13)	56(5)
C(112)	2929(28)	6227(20)	212(14)	62(5)
C(113)	2116(26)	5177(20)	349(14)	62(5)
C(114)	1237(26)	4823(19)	1066(13)	56(5)
C(115)	1223(25)	5552(17)	1703(12)	51(4)
C(116)	2049(24)	6714(17)	1575(12)	47(4)
F(1)	3870(16)	8085(11)	707(8)	69(3)
F(2)	3808(18)	6604(12)	−498(9)	87(4)
F(3)	2178(19)	4377(13)	−254(9)	91(4)
F(4)	350(17)	3739(12)	1204(8)	75(3)
F(5)	401(15)	5157(11)	2433(7)	65(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

in the reverse phase was carried out. Cluster **I** and its parent cluster $[Os_3(CO)_{11}(CH_3CN)]$ were incapable of separation when 10% MeOH/90% CH_3CN was used as the mobile phase. However, when 10% H_2O/90% CH_3CN was used, satisfactory separation of the mixture of clusters was observed (Fig. 2). The order of elution was as follows: $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$ (t_R, 11.98 min); $[Os_3(CO)_{11}(CH_3CN)]$ (t_R, 12.54 min); $Os_3(CO)_{12}$(t_R, 14.06 min);

TABLE 2

Selected bond lengths (Å) and bond angles (°) for $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$

Os(1)–Os(3)	2.917(1)	Os(1)–N(1)	2.134(14)
Os(1)–C(13)	1.952(21)	Os(2)–N(1)	2.084(11)
Os(2)–Os(3)	2.888(1)	Os(2)–C(21)	1.924(28)
Os(2)–O	2.075(11)	N(1)–C(116)	1.506(25)
N(1)–O	1.944(27)	Os(3)–C(31)	1.898(19)
Os(3)–Os(1)–N(1)	81.5(3)	Os(3)–Os(2)–N(1)	83.0(4)
N(1)–Os(1)–C(13)	93.9(8)	N(1)–Os(2)–O	40.4(5)
Os(3)–Os(2)–O	86.2(4)	Os(1)–N(1)–Os(2)	116.7(7)
Os(1)–N(1)–C(116)	117.9(8)	Os(2)–N(1)–O	69.5(6)
Os(2)–N(1)–C(116)	120.3(9)	Os(2)–O–N(1)	70.1(7)

and $[Os_3(CO)_9(\mu_3\text{-}NC_6F_5)_2]$ (t_R, 23.35 min). The identity of each of the four chromatographic peaks was established by determining the absorption spectra (Fig. 3) of the eluants using the photodiode array detector and an evaluation programme 'Data Evaluation Pack' for the HP-85B computer. The acquired spectra were then compared with those obtained separately with a Perkin–Elmer Lambda 9 UV–vis–near-IR spectrophotometer and the identities of the peaks were thus confirmed.

The purity of the chromatographic peaks may be checked using the Data Evaluation Pack programme through determination of the ratios of the heights of the chromatographic peaks monitored at 230 and 254 nm (Fig. 2). As a constant ratio of the two signals across a peak elution profile indicates peak purity, it can be said that each chromatographic peak observed consists mainly of a single cluster.

Experimental

C_6F_5NO [5] was prepared as previously described and $[Os_3(CO)_{11}(CH_3CN)]$ [6] was prepared as described in the literature. THF was dried by distillation from sodium and benzophenone. The infrared spectrum was recorded on a Perkin–Elmer 983G infrared spectrophotometer. ^{19}F NMR data were obtained on a JEOL FX 90Q Fourier Transformation NMR spectrometer. Elemental analyses for C and N were conducted by the Microanalytical Laboratory in the National University of Singapore while the F analysis was undertaken by Dr Beller of Mickroanalytisches Laboratorium, 34, Gottigen, Theaterstrasse 23, Postfach 109, West Germany. HPLC separation of the clusters was achieved using a Hewlett–Packard HP 1090 Liquid Chromatograph with a HP-85B personal computer, 3392A integrator and a 1040A diode array detector. The UV spectra were recorded on a Perkin–Elmer Lambda 9 spectrophotometer.

Preparation of $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$

Blue C_6F_5NO (22 mg, 0.11 mmol) in 15 ml THF was added dropwise to a solution of $[Os_3(CO)_{11}(NCMe)]$ (84.8 mg, 0.09 mmol) in 10 ml THF

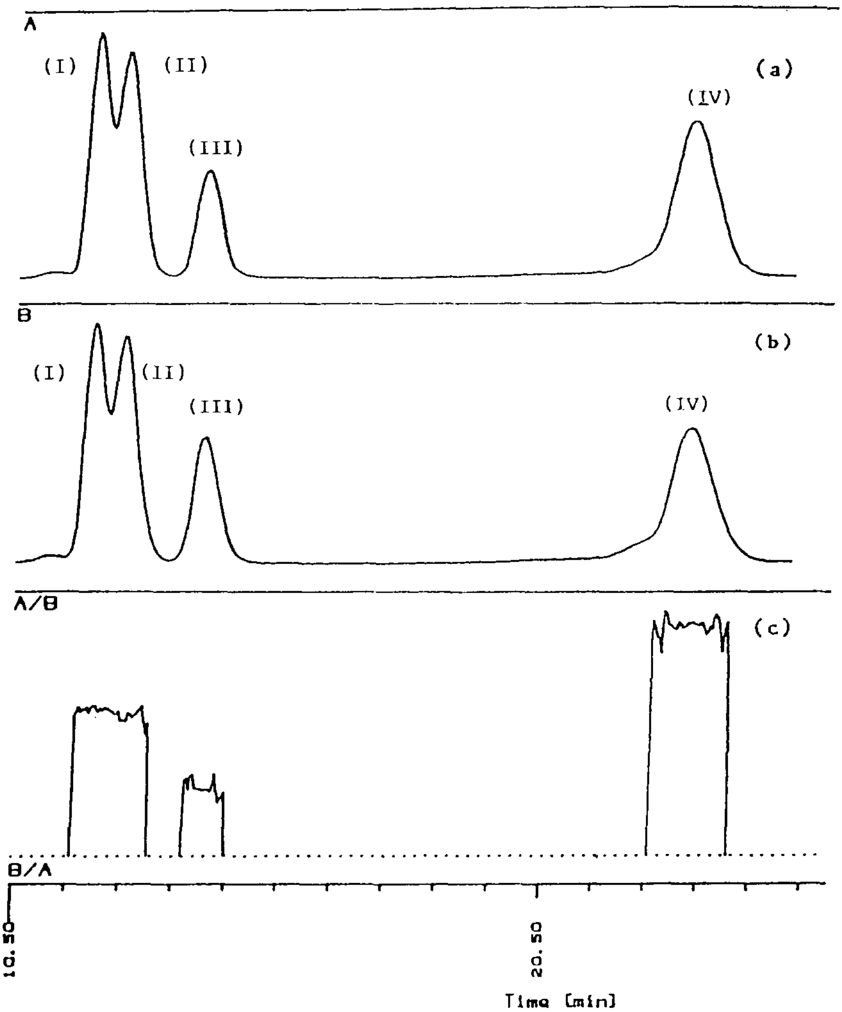

Fig. 2. HPLC chromatogram of $Os_3(CO)_{11}(\mu\text{-}ONC_6F_5$ (I), $Os_3(CO)_{11}(CH_3CN)$ (II), $Os_3(CO)_{12}$ (III) and $Os_3(CO)_9(\mu\text{-}NC_6F_5)_2$ (IV) at (a) 230 nm and (b) 254 nm; (c) is the ratio plot of signals at the two wavelengths. Mobile phase, 10% water + 90% acetonitrile; column, Lichrospher-100 RP 18, 250×4 mm, 10 μm; flow rate, 0.5 ml min^{-1}; temperature, ambient.

over a period of 20 min. After which, excess solvent was removed by rotary evaporation. The residue was chromatographed on silica using 20% dichloromethane/80% hexane as eluent from which a major yellow band was obtained (R_f, 0.21). Evaporation of solvent yielded $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$ (13.7 mg, 14% yield) as a yellow solid. Analysis: Found: C, 19.43; N, 1.58; F, 9.0%. $[Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)]$ requires: C, 18.97; N, 1.30; F, 8.83%.

Crystal structure determination

Crystals suitable for X-ray structural analysis were obtained from hexane/dichloromethane. A yellow crystal of 0.30×0.35×0.40 mm dimensions was

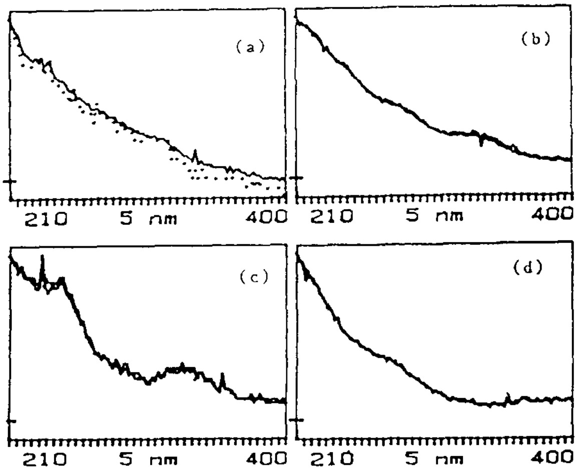

Fig. 3. UV absorption spectra for (a) $Os_3(CO)_{11}(\mu\text{-}ONC_6F_5)$, (b) $Os_3(CO)_{11}(NCCH_3)$, (c) $Os_3(CO)_{12}$ and (d) $Os_3(CO)_9(\mu\text{-}NC_6F_5)_2$ obtained using the photodiode array detector on HP 1090.

used for data collection on a Siemens diffractometer R3m/V by an ω scan technique ($3.0 \leqslant 2\theta \leqslant 50.0°$). Crystal data for **I**: $[C_{17}NO_{12}F_5Os_3]$; triclinic, P|; $a = 7.7080(10)$, $b = 9.482(2)$, $c = 17.079(3)$ Å; $\alpha = 81.760(1)°$, $\beta = 79.520(2)°$, $\gamma = 74.060(4)°$; $V = 1175.8(4)$ Å^3; $Z = 2$; $D_c = 3.042$ g cm^{-3}; MoKα radiation, $\lambda = 0.71073$ Å, μ(MoKα) = 163.14 cm^{-1}; $T = 25$ °C. Of 4444 measured data, 3221 were considered observed with $F_0 \geqslant [4\sigma(F_0)]$. The structure was solved by direct methods and refined by Fourier and least-squares syntheses with anisotropic temperature factors and anomalous scattering corrections made [7], leading to $R(F) = 6.06\%$, $R(wF) = 6.76\%$, Goodness-of-Fit = 2.45, $\Delta/\sigma = 0.001$, $\Delta/\sigma_{max} = 0.004$. SHELXTL software (G. M. Sheldrick, Siemens, Madison, WI) used for all computations. An empirical (psi-scan) absorption correction was performed.

Acknowledgements

We thank the National University of Singapore for a research grant. One of us (K. K. Ong) is grateful to the university for a research scholarship.

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